

DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Twentieth Six-Month Report  
for the period  
1 January 1973 to 30 June 1973

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## I. INTRODUCTION, ABSTRACT, AND SUMMARY

This report will cover the work performed from 1 January 1973 through 30 June 1973 on Grant NGL 03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption system for control and separation of gases.

Results to date have included detectors for  $O_2$  and  $H_2$  under partial vacuum conditions (publications 1, 3, 4). Experiments on detectors for use at high pressures began in 1966; and systems for CO,  $H_2$ , and  $O_2$  were reported in 1967 and 1968 (publications 8, 11). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (publications 11, 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film, was shown to be satisfactory when properly used. This technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the non-reflective nature of this film (publication 13).

During the period from 1969 through 1971 the Carbon Monoxide Detector, first demonstrated on this NASA program (publication 8), was refined and improved for use by the Department of Health, Education and Welfare. The unit is now under evaluation at the Cincinnati office of the National Institute for Occupational Safety and Health (NIOSH).

In 1969 studies began on a Corona Discharge Detector for water vapor. This system was shown to be rapid in response, suitable for continuous low operation, and reasonably linear in output (on a logarithmic plot) from 10 percent relative humidity to 95 percent relative humidity. A program to develop this detector for hydrological applications began in 1970 but was temporarily dropped because of limited user interest.

In 1970 we began an investigation of the catalytic oxidation of various gases, i.e. CO, NH<sub>3</sub>, and H<sub>2</sub> over metallic catalysts. We demonstrated that the rate of reaction could be observed and controlled in terms of the exoelectron emission from the catalyst (publication 16).

In 1971 this study was directed to the extended monel metal catalysts used for auto exhaust emission control and for spacecraft atmospheric purification (publication 20).

In 1971 we began the study of a new technique for analysis of solid materials. This system involved heating or grinding the substance and observing the induced exoelectron emission. This effect is known as Temperature Stimulated Exoelectron Emission (TSEE), and a number of applications of TSEE have already been demonstrated. We have investigated the use of this technique for analysis of minerals, levitation of dust by electrostatic repulsion, and investigation of dust-induced lung injury. This latter application relates directly to the industrial health environment where silicosis is a serious problem. There appears to be a direct connection between the exoelectron emission we observe after grinding and the ability of the ground silica for induction of silicosis. The results of this work are being evaluated for possible support by various organizations.

## II. SUMMARY OF WORK IN THE PAST SIX MONTHS

### A. Catalytic Studies

The original program involved a demonstration that exoelectron emission could be used to monitor and partially control the rate of a catalytic reaction; the details of the work have appeared in the literature (publication 16). We have expanded this work to demonstrate

that the technique can be used to monitor the monel catalyst that is used for automotive smog reduction. A Letter to the Editor discussing this work has been accepted by the *Journal of the Society of Automotive Engineers* (publication 20).

We hope to continue this program by building a catalytic reactor that will operate at atmospheric pressure. This will allow us to simulate the actual situation that occurs in an automobile smog control system. It is interesting to note that the smog control system used for automotive work is quite similar to that used for contaminant removal in spacecraft. The catalytic reactor that we hope to build will be able to simulate the conditions used in a spacecraft catalyst system [1].

#### B. Dust Grinding and Electrification Studies

Our first experimental studies in this area related to measurement of rate grinding of industrial minerals. This work has been reported recently (publication 18). The work is continuing with the support of the Tucson Anaconda Laboratory.

Our recent experimental studies are discussed in detail in Appendix A where we reproduce a paper given at the Boston 1973 meeting of the American Industrial Hygiene Association. This paper will appear as a regular publication in the *Journal of the AIHA*. The results will be reviewed quickly at this point to indicate what has been done and where we hope to go in the future.

In the last six months we have been looking into the dust-charging problem in more detail for two reasons: The first relates to the question of dust levitation on Mars; here we note that if freshly ground silica does in fact emit a large number of exoelectrons, we must expect that the silica will acquire a substantial electrostatic charge. This charging phenomenon might well produce some glow discharge effects in the low-pressure Martian atmosphere. Some recent experiments under simulated Martian dust cloud conditions have indicated that significant charging and glow-discharge phenomena might occur on Mars [2].

The levitation phenomenon requires that dust charging be highly asymmetrical because a cloud of particles having equal numbers of positively and negatively charged particles would self neutralize quite rapidly. In view of the intensity of Martian dust storms photographed by Mariner 9 [3] we might expect asymmetrical charging to occur. Field studies by Kamra have shown that if certain types of dust are blown about, the resultant charge distribution is very asymmetrical and largely negative [4]. Laboratory work by Kunkel has shown that silica dust will charge asymmetrically if ground in the presence of heavy metals [5]. This agrees exactly with our own experiments on exoelectron emission, after grinding; and it is interesting to estimate the effect of such charging on dust levitation. If we consider a particle of silica with a diameter of one micrometer and assume it to have acquired the level of electrostatic charge observed

by Kunkel [5], we can compare the electrostatic force in the Earth's field gradient to the effect of gravity. The ratio is given by:

$$\frac{\text{Electrostatic Force}}{\text{Gravity Force}} = \frac{en\epsilon}{mG} = 2.3 \cdot 10^{-4} \epsilon$$

The values of the various parameters are:

$\epsilon$ (Field Gradient)	= volts/meter
e (Electronic Charge)	= $1.6 \cdot 10^{-19}$ coulombs
n (Number of Charges)	= 14
m (Mass of 1 micron Particle)	= $10^{-15}$ Kg
G (Acceleration of Gravity)	= $9.81 \text{ M}/(\text{sec})^2$

The major question is: What value to choose for  $\epsilon$ , the electrostatic field gradient. The normal clear-weather value is 100 volts per meter; in thunderstorms or dust devils values of  $10^4$  volts per meter have been reported.

It is clear that for any value of  $\epsilon$  greater than 1000 volts per meter dust particles will be levitated almost indefinitely. If there is an appreciable atmospheric effect, it will further slow down the rate at which dust particles fall out. This conclusion is borne out by air pollution studies that indicate a significant level of one micron dust which does not disappear from the atmosphere even in the clearest of atmospheric conditions [6]. Adapting this result to conditions on Mars is difficult because we do not have data on

the natural electrostatic field of Mars. Nevertheless, the immense dust storms observed on Mars are a strong indication that significant dust levitation might be present.

In our recent studies we have used a continuous grinding system where the material (silica sand) goes through an air impact grinder, up to a dust chamber, and then back down to the grinder again. After about two hours of operation the sand is ground from the initial 60 mesh (250 micrometers) to below 20 micrometers. Samples are drawn from the dust chamber into an Anderson 2000 Impact Sampler and separated by size. We have modified the sampler to permit observation of the exoelectron emission from the dust at every level in the sampler. The results to date indicate that the one micrometer dust does in fact emit a significant exoelectron current which suggests that it has acquired an electrostatic charge. It is interesting to note that the charge is negative rather than positive as one would expect from a particle that is emitting electrons. Apparently the dust particles have a large number of electrons on their surfaces after grinding, and the fraction emitted is not large enough to change the net charge from negative to positive.

In other studies we have investigated the effects of metallic impurities on the exoelectron emission phenomenon. There seems to be no question that the addition of trace quantities of aluminum reduces the emission to almost zero. The addition of a similar quantity of

iron raises the rate of emission, and this may be significant in view of the many suggestions of iron oxides on the surface of Mars. If appreciable quantities of iron do exist on Mars, we can expect significant asymmetrical charging of dust during wind storms. This problem is significant for understanding of the Martian atmosphere and may have to be considered in the design of planetary landing vehicles. We plan to begin studying the effect of these metallic impurities on the exoelectron emission from silica dust of various sizes. This will allow us to estimate how significant the impurity effect is for the one micrometer size dust that is most likely to be levitated by electrostatic effects.

The second area of interest in our dust investigation involves the possible connection between the charge acquired by the dust and the effect of the dust on human lung tissue. In our last report we suggested that such a connection existed because the exoelectron emission from ground silica was so large and lasted for such a long time after the material had been ground. In the last six months we have begun studies of the effect of ground silica on red blood cells (RBC) to assess the ability of silica to lyse the RBC. This type of test, which involves the separation of RBC from whole human blood, is the one generally used for investigation of substances thought to be effective as lung irritants. Again, the details are given in Appendix A. Here we shall simply comment on the results obtained to date. First, we have shown that ground silica is more effective

for lysis of RBC than other industrial dusts, i.e., flour, talc, starch, etc.

The effect of metallic impurities is quite significant; if one percent aluminum is added to the silica during grinding, the lytic ability of the silica is reduced almost to zero. If an equal quantity of iron is added, the lytic action is greatly increased. This agrees directly with the exoelectron studies discussed earlier.

Second, we have essentially settled the question of the silicotic damage capability of freshly ground versus aged silica. In an industrial environment where there is significant aluminum present, the silica is rendered inert rather quickly, even when there is iron in the environment. In the laboratory where silica is stored under clean conditions, it remains lytically active for weeks, if not months.

Third, we have shown that the sequence in which silica is attracted to a RBC - causes hemolysis and then moves to another RBC - involves a protein reaction. The protein coating phenomenon is part of the normal human defense mechanism and may provide a key to the eventual development of a blood test for early human silicosis. The advantages of a test of this type for reducing the present rate of industrial injury by silica are so large that we are putting a significant amount of effort into this area.

In the next six-month period we will continue the RBC study and add to it a series of experiments on living systems (rats). We

hope to demonstrate that a blood test for early silicosis can be developed and that the presence of aluminum in trace quantities provides protection against the development of silicosis.

C. Other Activities in the Laboratory

The ARPA sponsored studies on the relationship between fatigue and subsequent exoelectron emission are continuing with Air Force support. We have shown that if a metal is fatigued to some fraction of its total life and then heated gently, it will emit exoelectrons. This electron current can then be related to the fatigue history of the specimen. We have also developed an exoelectron system for scanning along an aircraft structure to detect cracks or crack growth during flight. This technique has been extended to the monitoring of stress relief annealing processes. The first results of these studies have been published (publication 17), and later results will appear in March, 1973 (publication 19).

The Laboratory is now recognized as a center for research on exoelectron phenomena, and on 4 - 5 September 1973 Professor Hoenig will give a paper reviewing the various exoelectron studies at the Tokyo Symposium on New Trends in Nondestructive Phenomena. This trip will be made at the invitation and expense of the Japan Industrial Planning Association. Professor Hoenig is one of two Americans invited by the JIPA. A copy of the talk is attached as Appendix B.

It is most important to note that the research involved was supported by a number of agencies, including NASA, the Air Force, HEW, and the Engineering Experiment Station of the University of Arizona. The exchange of funds and equipment provided by the various programs has been of significant aid in many facets of this research. In all of these efforts the funding from the NASA grant has allowed us to support important programs during the intervals between other research grants. Without this long-term assistance many of our studies would never have been finished.

Another use of Laboratory facilities occurs in connection with two courses taught by Professor Hoenig in Electronics and Instrumentation for graduate students in the Zoological, Geological, and Medical Sciences. These students use the Laboratory and its apparatus for demonstrations and simple projects. Again, this would be impossible without the long-term support we have received from NASA.

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### III. PERSONNEL

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M. S., 1963; Ph.D., California Institute of Technology, September 1969. Research Associate, California Institute of Technology.
2. George Rozgoni, Ph.D., 1963; Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
3. Donald Creighton, Ph.D., 1964; Professor, University of Missouri, Rolla. (Partial NASA support.)
4. Col. C. W. Carlson, M. S., 1965; Active duty, U. S. Army.
5. Melvin Eisenstadt, Ph.D., 1965; Professor of Mechanical Engineering, University of Puerto Rico, Mayaguez, P. R.
6. John Lane, M. S., 1968; Philco Ford Company, Tucson.
7. William Ott, M. S., 1970; Burr-Brown Research, Tucson. (Partial NASA support.)
8. Richard Pope, M. S., 1970; Hewlett-Packard Corporation, Palo Alto, California.
9. Robert Goetz, M. S., 1972; Ph.D. Candidate, Biomedical Engineering, University of Arizona.
10. Freedoon Tamjidi, M. S., 1972; Westinghouse Company, Phoenix, Arizona.

### IV. PUBLICATIONS GENERATED TO DATE BY RESEARCH ON THIS GRANT

#### S. A. Hoenig and Others

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2. "Protection of Copper in High Temperature Air," Rev. Sci. Instr., 35, 904 (1964).

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4. "Change in the Thermionic Emission Current of Palladium Due to Chemisorption of Atomic and Molecular Hydrogen," J. Chem. Phys., 45, No. 1, 127-132 (July 1966), with M. Eisenstadt.
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13. "Replication Versus Metallization for Interference Microscopy of Thin Films," J. Vacuum Sci. and Technology, 5, 125-126 (July/August 1968), with J. Lane
14. "Ion and Electron Currents from Hot Filaments: Effects of Alloying on Electron Emission," Solid State Tech., 11, No. 12, 53 (December 1968), with R. Pope.

15. "A Study of Stress Corrosion Cracking of U-10% Mo Wires," in Applications of Field-Ion Microscopy in Physical Metallurgy and Corrosion, edited by R. F. Hochman et al., Georgia Institute of Technology, Atlanta (December 1969), with H. Sulsona.
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20. "Application of Exoelectron Emission to Monitoring the Reaction of CO and NO over Hot Monel," accepted by the Journal of the Society of Automotive Engineers.

APPENDIX A

EXOELECTRON EMISSION FROM  
FRESHLY GROUND SILICA  
AND  
THE INDUCTION OF  
SILICOSIS

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## ABSTRACT

We have investigated the exoelectron emission from silica and silica minerals during and after grinding. It is possible to follow the rate of grinding by this technique; the post-grinding electron emission is strongly dependent upon the silica content of the ground material and contamination by trace metals, i.e. iron and aluminum.

This post-grinding electron emission may have a direct correlation with the induction of pulmonary lesions associated with silicosis. To investigate this relationship, we have used red blood cells (RBC) as a model system for studying the effects of silica on biological membranes. The silica-RBC interaction results in lysis of the RBC which is detected as a change in optical density. We have shown that silica particles adsorb protein during the process of damaging membranes and are rendered inactive for lysis of RBC. Selective removal of this adsorbed layer reactivates the membrane-damaging properties of the silica particles. The presence of a trace amount of aluminum substantially decreases and a trace amount of iron increases the rate at which silica dust attacks RBC.

We present a rationale and supporting evidence to explain the common observation that there is a time-dependent decrease in the pathogenicity of silica dust in an industrial environment while no such time-dependent decrease is seen in controlled laboratory experiments.

## INTRODUCTION

Silicosis is the medical term for a variety of industrial diseases involving the lungs of workers associated with mining, milling, or grinding

operations. Silicosis is usually the result of prolonged inhalation of free, crystalline silica particles of a restricted size range. In man there is generally a long latent period of exposure prior to recognizable clinical or radiographic lung changes, and frequently the changes continue to progress after exposure ceases.

A general correlation exists between length and intensity of exposure on the one hand and frequency and severity of pulmonary changes on the other; but this predictability is only statistical, and there is great variability in the individual human response to silica. This may be partially due to the fact that the etiology and pathology of silicosis are not completely understood. This in turn makes it difficult to separate the effects of particle size, impurity content, crystalline state, and time lapse between particle generation and inhalation.

Silica, like any particulate material reaching the terminal air spaces, is subject to the two main clearance or cleansing mechanisms of the lung. First, the sticky blanket of mucus propelled by the ciliary activity of airway cells toward the mouth; and second, engulfment by macrophage cells, which then generally leave the air spaces to enter the interstitial tissue of the lung. Silicosis appears to be a consequence of macrophage injury and death induced by the engulfed silica particles, Nash et al (1). The injured cells release toxic chemicals (generally enzymes) which stimulate inflammation and fibrosis in the pulmonary interstitium. The precise sequence of events leading to the silicotic lesion is not known, although injury to organelle membranes by ingested silica is probably an important factor.

There are strong clinical and experimental immunologic implications

in the pathogenesis of silicosis. Susceptibility to tuberculosis seems to be enhanced by the presence of silicosis. In turn, co-existent tuberculosis often appears to accelerate the progression of the silicotic lesion, Spencer (2). A peculiar, rapidly progressive form of silicosis following relatively small dust exposures is seen in some individuals who have or who subsequently develop rheumatoid arthritis, a disease in which several immunologic abnormalities have been demonstrated, Davis et al (3). Experimental silicosis in animals is enhanced by administration of immunologic adjuvants, Zadi (4).

The consequences of silicotic lesions include the destruction of air-bearing parenchyma and the vascular bed with loss of lung volume and mismatching of ventilation and blood perfusion, Zadi (5). The loss of lung compliance ("stiffening" of the lung) increases the work of breathing and causes an eventual inadequacy of gas exchange with subsequent heart failure and death.

The effectiveness of silica dust in inducing silicosis seems to be dependent upon the time lapse between dust generation and inhalation. It is occasionally suggested that "old silica dust is relatively harmless; freshly ground silica dust is very dangerous". This was proposed by Heffernan (6) in 1935 and is corroborated by the frequent observation that in coal mines the roof bolters, who drill directly into rock and are exposed to freshly ground silica, are very likely to develop silicosis. [The observation that silica obtained from cadavers is still fibrogenic Gardener (7) might be explained in terms of the "reactivation" of the silica by the techniques used to remove it from the lung tissue].

There is other evidence that the crystal form (quartz, tridymite, etc.) and impurity content of the silica have an influence upon the in-

duction of silicosis, Zadi (8). However, to date no explanation of these effects has been offered. We shall suggest that the induction of silicosis is related in some way to the surface structure of the silica or to the exo-electrons emitted by the silica after it has been ingested into the lung. The phenomenon of macrophage destruction discussed above might be a chemical effect of the low energy exoelectrons or it may be due to surface reaction process where the electron current can serve as an indication of potential injury.

#### EXPERIMENTAL STUDIES AT THE UNIVERSITY OF ARIZONA

Because of the complex nature of this problem, we have run concurrent studies in two areas. The first is a study of the exo-electron emission from silica and other miscellaneous industrial materials during and after grinding. In this study we hoped to demonstrate that the hazardous nature of industrial materials could be evaluated in terms of their exo-electron emission.

The second study made use of red blood cells (RBC) as a model for assaying the destructive effects of silica on lung tissue. It was our expectation that this technique would permit rapid evaluation of the question of toxicity of fresh versus old silica and give insight into the actual mechanism for this specific reaction.

##### I. Grinding Experiments.

Our original studies were oriented toward following grinding and milling processes by means of the electron emission (called exoelectron emission) that is associated with the creation of new surface by fracture. This exoelectron work was based upon the earlier studies of Kramer (9, 10) who suggested that when any rock-like material was crushed, the newly generated surface would be an electron emitter even at room temperature. This proved to be true, and we were able to demonstrate that the milling rate of a wide variety of industrial materials could be monitored by means of the emitted exoelectrons.

and that the level of emission was characteristic of the mineral involved. Typical apparatus and results are shown in Figures 1, 2, and 3. The detector was a brass rod with a glass insulator and an outer stainless steel cover. The one quart jar was used as a ball mill with porcelain balls. (We have found it necessary to use a fresh jar and balls each time we change materials; otherwise cross contamination is a serious problem.)

The data of Figures 2 and 3 show the change in average particle size and the variation in exoelectron emission with time. The parallel curves indicate that a correlation exists between the rate of grinding and the rate of exoelectron emission. The detailed results of this experiment have been published recently (11). This work is continuing with the cooperation of the Tucson Laboratory of the Anaconda Co.

The application of this work to silicosis arose during a conversation with Mr. John Crable of the National Institute for Occupational Safety and Health (NIOSH), Cincinnati, Ohio. After discussing the problem, the authors suggested that exoelectron emission might be applicable to the silica problem in terms of the following mechanism:

1. Assume that when silica is ground or crushed, it begins to emit exoelectrons at a current level which allows it to be distinguished from other "rock-like" materials. This emission will decay with time but should be observable for hundreds of hours after grinding has ceased.
2. If this idea is correct, it should be possible to evaluate the relative silica content of an ore by monitoring the exoelectron current during the grinding process. If one has samples of various previously crushed materials, it may be possible to analyze them in terms of their silica content by heating them and observing the exoelectron emission.
3. Let us assume for the moment that the lung pathology observed in silica exposure is due to or correlates with the exoelectron emission that occurs after the dust has been ingested. This would fit in with the knowledge that the exoelectron emission decays with time, and the suggestion that freshly generated silica dust is most harmful, Boose (12).

The experimental studies at the University of Arizona began in February, 1971, on State Funds, with the objective of measuring the percentage of silica in a previously ground sample by heating the sample and observing the exoelectron emission. The dust samples for this study were provided by Mr. John Crable of NIOSH. The apparatus is shown in Figure 4. For a test, the dust was loaded into the holder and heated to 400°C over a 16-minute period. The raw data in terms of exoelectron current versus time are shown in Figure 5; the data are replotted in Figure 6 as exoelectron current level (after 8 minutes) versus silica content. There appears to be a correlation, and we suggest that if this relationship can be confirmed, the possibility exists for developing a simple test for silica in ground materials. Federal agencies involved in industrial health are facing the problem of testing thousands of dust samples for their silica content, and this technique has the potential for being easily automated. There is some variation if the minerals contain appreciable water, and this may require the ore to be treated before a test for silica is run.

In another series of experiments, we used a suction system, as shown in Figure 7, to pull off a sample of the dust from a ball mill. The data for rock salt and silica sand are shown in Figure 8. It was necessary to normalize the data in terms of the initial current because the rate of grinding of the two materials was so different. The most significant factor is the rate of decay of the exoelectron current when the flow of dust ceases. The rock salt exoelectron current decays very rapidly while the silica exoelectron current decays only very slowly. This is in agreement with our suggestion that silica continues to emit electrons for a long time after it enters the human lung.

More data of this type are shown in Figure 9 where the decay with time of the exoelectron current was followed for many hours. The 36 per cent silica material has a lower initial current than the 100 per cent silica material, and the decay of the 100 per cent silica current is much slower. Again, this is in agreement with our suggestion of a correlation between exoelectron emission and silicosis.

Another aspect of the silicosis problem related to the numerous reports in the literature, Schepers (13) indicating that the presence of aluminum had a prophylactic effect on the induction of silicosis. These reports and other scattered suggestions that iron had a potentiating effect on the disease, suggested that we run ball milling experiments with iron or aluminum powder added to the silica sand. Typical results are shown in Figure 10. There seems to be no question that iron increases the observed exoelectron currents and aluminum decreases them. This data is in agreement with our suggestions of a correlation between exoelectron emission and silicosis. In another section of this paper we will discuss the red blood cell data that provides further evidence for this correlation.

For the next experiment, we decided to grind the silica sand in one container and measure the exoelectron emission in a separate set-up. This allowed us to grind the sand under wet or dry conditions and then measure the current in a simple and easy to clean system. Sixty mesh silica sand was ground with mortar and pestle, and 100-mg samples were loaded into a 25 mm steel planchet. The exoelectron current from the ground material was observed with the apparatus shown in Figure 11. The results were somewhat erratic because of the delay in loading the planchet, but some definite trends can be observed in Figure 12. One curve shows the decay of the exoelectron current from dry-ground silica sand; the other two

curves show the effect of wet grinding and the addition of one per cent aluminum powder during dry grinding. Once again the aluminum addition has reduced the exoelectron emission.

The fact exoelectron emission can be observed after wet grinding is another indication that electron emission can occur even after silica dust has been ingested into the moist environment of the human lung.

Another part of the program involves a study of the exoelectron emission from ground silica as a function of particle size. If the electron emission is related to the induction of silicosis, the respirable particles, below 2 micrometers in diameter, must emit a significant fraction of the current observed from a mixture of ground silica particles. To investigate this question, we have constructed a dust chamber and analysis system (figure 13). The dust is ground and circulated by a Trost Corp GEM-T air-driven impact grinder. Dust samples are drawn from the system into an Anderson sampler.\* The Anderson sampler is an impaction device that we have modified to permit a continuous measurement of the exo-electron current from each level of the sampler. Ideally, we would want to measure the current from each level of the sampler at the same time. However, the cost of this approach would be quite high and we chose to design and build an automatic sequential switching system. The system switches the signals from the various levels

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\* The cooperation of the Trost Corp. of Newton, Penna. and the Anderson-2000 Corp. of Atlanta, Ga. in allowing us to purchase this equipment at reduced cost is greatly appreciated.

of the sampler into the picoammeter and recorder. Each signal is "on" the recorder for 30 seconds to permit stabilization; after 30 seconds the system switches to the next level in the sampler. Operation is continuous and completely automatic even at current levels of  $10^{-11}$  amps. A paper describing this system is being prepared for the Review of Scientific Instruments.

The first experiments with this system indicate that substantial exo-electron emission is observed from ground silica particles with diameters below 2 micrometers. Calculation of the emission rate per unit area of weight will require careful measurement of the quantity of dust deposited at each level of the sampler.

In a second experiment we propose to measure the dust charge spectrum using the well-known parallel plate precipitator, Walkenhorst (15). The device is shown in Figure 14; as the stream of dust-laden air passes between the plates, the charged dust particles are drawn off to the plates. The plate currents are then a measure of the total number of particles of each polarity. The plate potential required to collect the charged particles is a function of the particles charge itself. It should be possible to observe the entire dust charge spectrum using this device. If the plate currents are too small to measure electrically, we will use optical detection techniques to measure the dust flow in and out of the precipitator. If the collector plates are coated with a sticky material, the plates can be examined after a run. It will be interesting to see if, in a mixture of dust, the various materials charge to different polarities.

## II. Red Blood Cell Experiments.

The events leading to silicotic injury appear to be as follows:

Silica dust is inhaled and some fraction is deposited on the pulmonary surfaces. The dust particles are then engulfed by lung macrophages followed by sequestration of the dust in their lysosomes. By some as yet not understood mechanism, the lysosomal membrane is injured by the silica particle and this violation of the lysosomal membrane results in the eventual death and lysis of the macrophage, Allison et al (16). It has been reported that the newly released silica particle is again taken up by another macrophage and that the same sequence of events, culminating in death and lysis, ensues after each engulfment, Heppleston (17), Vigliani (18), Pernis (19). A number of workers, ourselves included, are of the opinion that the primary pathogenicity of silica is due to its damaging the lysosomal membrane in which the silica particle is sequestered, Stalder (20), Nash (1), Stalder (21).

The red blood cell (RBC) has been used as a model system for studying the mechanism by which silica damages biological membranes. A measurement of released hemoglobin from damaged RBC's is commonly used as a convenient estimation of the amount of damage sustained by the RBC membranes, Stalder (21), Allison (16), Nash (1).

In our studies we have relied on freshly drawn and thoroughly washed human RBC's suspended in isotonic sodium citrate - sodium chloride buffer at pH 7.4. The general experimental procedure involves preparing a suspension of RBC's such that when 4 volumes of H<sub>2</sub>O are added, the optical density at 4160 Å is about 0.8. A buffered suspension of silica powder (240 mesh) is prepared such that when 2 volumes are added to 2 volumes of buffer plus one volume of RBC suspension and this composite suspension centrifuged (1,000 g, 5 minutes, 25°C) the supernatant has an optical density at 4160 Å of about 0.4.

The effect of different agents on the lytic capacity of silica was tested by substituting a buffered suspension of the agent for the two volumes of buffer in the above described silica-RBC mixture. The lytic capacity of the silica is proportional to the optical density of the supernatant after centrifugation. This system permits the experimenter to observe the amount of lysis and evaluate the lytic capacity of any silica mineral. By doing a few "blank run" experiments, it is feasible to determine the "natural rate" of lysis and subtract this "natural rate" of lysis from the effect observed with silica suspensions.

In the first experiment we hoped to answer the question of whether freshly ground silica is more pathogenic than "old" silica dust. Subjective observations seemed to favor the theory that freshly ground silica is substantially more dangerous than aged silica dust. A typical observation of this sort is that miners exposed to very fresh dust, i.e. roof drillers, are more prone to silicosis than other workers who are exposed to equally high dust concentrations but under conditions where the dust has aged to some extent. Contrary to these non-quantitative and subjective observations is firm data showing that aged (over 20 years) silica dust can produce silicosis in experimental animals, Gardener (7).

In our studies we have found that the lytic capacity of ground quartz is essentially the same whether tested at 2 minutes after grinding or 5 weeks after grinding. The suggestion was then made that the difference between the industrial and the laboratory environment might explain the discrepancy between these conflicting observations. In an industrial environment the silica dust is exposed to a variety of contaminants which might well produce the observed "aging effect". Such an aging phenomenon might occur if newly formed silica surfaces were exposed to compounds which coated

or in some other manner inactivated the silica surface. In a laboratory setting such an inactivation process would not occur since reasonably pure preparations of silica are used and contact with contaminating compounds is severely limited.

We tested this "aging" hypothesis by long-term mixing of silica dust with a fine powder prepared from a heterogenous mixture of gravel. The lytic capacity of this artificially aged silica dust was compared with the lytic capacity of silica dust alone and of gravel dust alone. If no interaction occurred during the mixing of the dusts, then a given weight of silica dust mixed one to one with gravel dust should have lytic capacity intermediate between an equivalent weight of pure silica dust and an equivalent weight of pure gravel dust.

We found that if the lytic capacity of a given weight of silica is taken as 100 per cent then an equivalent weight of pure gravel dust had a relative lytic capacity of 90 per cent. If no inactivation (ageing) occurred during the mixing process, a one to one mixture of these dusts would be expected to have a relative lytic capacity of about 95 per cent. We found the "aged" dust mixture had a relative lytic capacity of only 74 per cent. The magnitude of this change is surprising and suggests some strong reaction between ground silica and gravel dust. This may be the industrial aging effect discussed above. This "industrial effect" is probably due to the presence of aluminum and its compounds in industrial environments. Aluminum comprises 8 per cent of the earth's crust and iron comprises about 5 per cent (oxygen at 49.5 per cent and silicon at 26 per cent are the only more abundant elements)! We believe that the dust in mines will, as a rule, contain high levels of compounds of aluminum and iron. It is

reasonable to suppose that the longer the newly formed silica surfaces are exposed to compounds containing these elements, the greater their possible effect.

In view of the suggestion that these elements, especially aluminum, can play an important part in the "dust-aging" phenomenon. We note again the many reports that the pathogenicity of silica dust is radically decreased by mixing it with small amounts (approx. 1 per cent w/w) of aluminum powder, Denny (22), King (23). We have noted above that the presence of a small percentage of aluminum powder, during the grinding of silica, strongly inhibited the normal emission of exoelectrons from the freshly ground silica particles.

Subjective observations seem to implicate low levels of iron contamination as a potentiator of silicosis. A typical observation of this sort is that, when iron or steel tools are used in crushing or grinding silica, the workers are much more prone to silicosis than when the crushing and grinding operations are carried out with tools composed of other metals. We noted above that the presence of 1 per cent, w/w, iron powder during grinding of silica greatly enhanced the normal emission of exo-electrons from the newly ground silica particles.

In view of the potentiating effects by these two agents on the pathogenicity, solubility, and electron emission properties of silica, we tested the potentiating effects of these agents on the capacity of silica to lyse RBC's. Figure 15 shows the effect of very small amounts of aluminum powder and iron powder on the lytic capacity of silica powder. In this experiment 1 g quantities of silica powder were thoroughly mixed

with from 1 mg to 20 mg of either iron or aluminum powder. These mixtures were suspended in buffer and the lytic capacity assayed as previously described. There is no question that the addition of aluminum decreases the lytic capacity of silica while iron has just the opposite effect. The experiments of figure 15 were repeated three times over a period of weeks and we feel confidence in the above conclusions. In view of the contral effects of aluminum and iron one might question whether silica would become more or less dangerous if both iron and aluminum were present. Preliminary experiments with the RBC system indicated that if iron and aluminum were present, to an equal degree, the effect was primarily that of aluminum suggesting that in industrial environments the effect of contaminants will be favorable. The silica will be rendered less harmful.

A second series of experiments was designed to answer the question of how silica interacts with biological membranes. The membrane-damaging capabilities of silica particles have been attributed to the ability of silica to abstract some component vital to the structural integrity of the membrane. Stalder and Stober (21) have suggested that silica lyses membranes by abstracting lipids, which are known to play a major role in membrane structure. Scheel (24) has proposed that silica's lytic capacity is due to its protein-binding property. Again, it is known that proteins play an important role in membrane structure. Hanahan has found that  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  are required for the structural integrity of RBC membranes (personal communication). A case could be made that silica (negatively charged in aqueous solutions) destabilizes membranes by abstracting cations from the membrane.

We have found that when silica powder is treated with an excess of RBC's (such that less than 100 per cent of the cells are lysed), the

treated silica is no longer capable of lysing RBC's, even after washing the RBC-treated silica with buffer or distilled water. We suggest that in this case the silica surface is saturated with some material that has been abstracted from the RBC's during the hemolytic process.

We felt that a knowledge of the identity of this coating material might give insight into the mechanism of lysis. Accordingly, we treated silica powder with an excess of RBC suspension. The silica was pelleted, washed with distilled water and then aliquots were treated with a number of agents in an effort to reactivate the lytic capacity of the silica. The chelating agent, ethylenediamine tetra acid (EDTA), was used to remove divalent cations. Various mixtures of chloroform and methanol and ammonium hydroxide were used to abstract lipids. Either pronase (a proteolytic enzyme) or sodium dodecyl sulfate (anionic detergent) was used to remove adsorbed protein. After each treatment, the lytic capacity of the silica was assessed by the RBC technique. The results are shown in figure 16. It is clear that the only agents effective in reactivating the lytic capacity of RBC-treated silica powder are those agents which remove or destroy proteins. Lipid solvents and divalent chelating agents have little or no reactivating action.

It has been reported that albumen-coated silica elicits a fibrogenic response similar to that of uncoated silica, Schepers (25). In contrast, we find that albumen-coated silica has a low lytic capacity but that the lytic capacity can be renewed by removal of the protein surface layer with either a protease or a detergent.

## CONCLUSIONS.

In view of our results and of the literature cited above, we would like to propose the following sequence of events leading to the silicotic lesion.

Silica particles which reach the alveoli are first coated by alveolar surface proteins. Macrophages engulf the protein-coated (non-lytic) particles followed by transfer of the engulfed particles to the lysosomal organelles. Once the protein-coated silica particle is within the lysosome, proteases in the lysosome begin digesting off the outer protein layer on the silica particle and thereby reactivate the particle for membrane lysis. This reactivated silica surface damages the encompassing lysosomal membrane and as a result lysosomal degradative enzymes are released into the cytoplasm of the macrophage. These free degradative enzymes attack the macrophage, culminating in death and lysis of the macrophage. At some stage during or after the violation of the lysosomal membrane by the reactivated silica surface, the silica surface is again coated with either macrophage or extracellular protein. Macrophage lysis results in a free protein-coated silica particle which can now be engulfed by another macrophage to repeat the cycle. Degradative enzymes along with other cytoplasmic contents released upon lysis of the macrophage, probably play a major role in initiating the fibrogenic response commonly seen in silicotic lung tissue.

## FUTURE STUDIES.

We propose to repeat these studies with macrophages (washed from rabbit lungs) in place of RBC. This will bring us closer to the real life situation in the human lung. Other studies will be devoted to examining the mechanism by which silica lyses membranes.

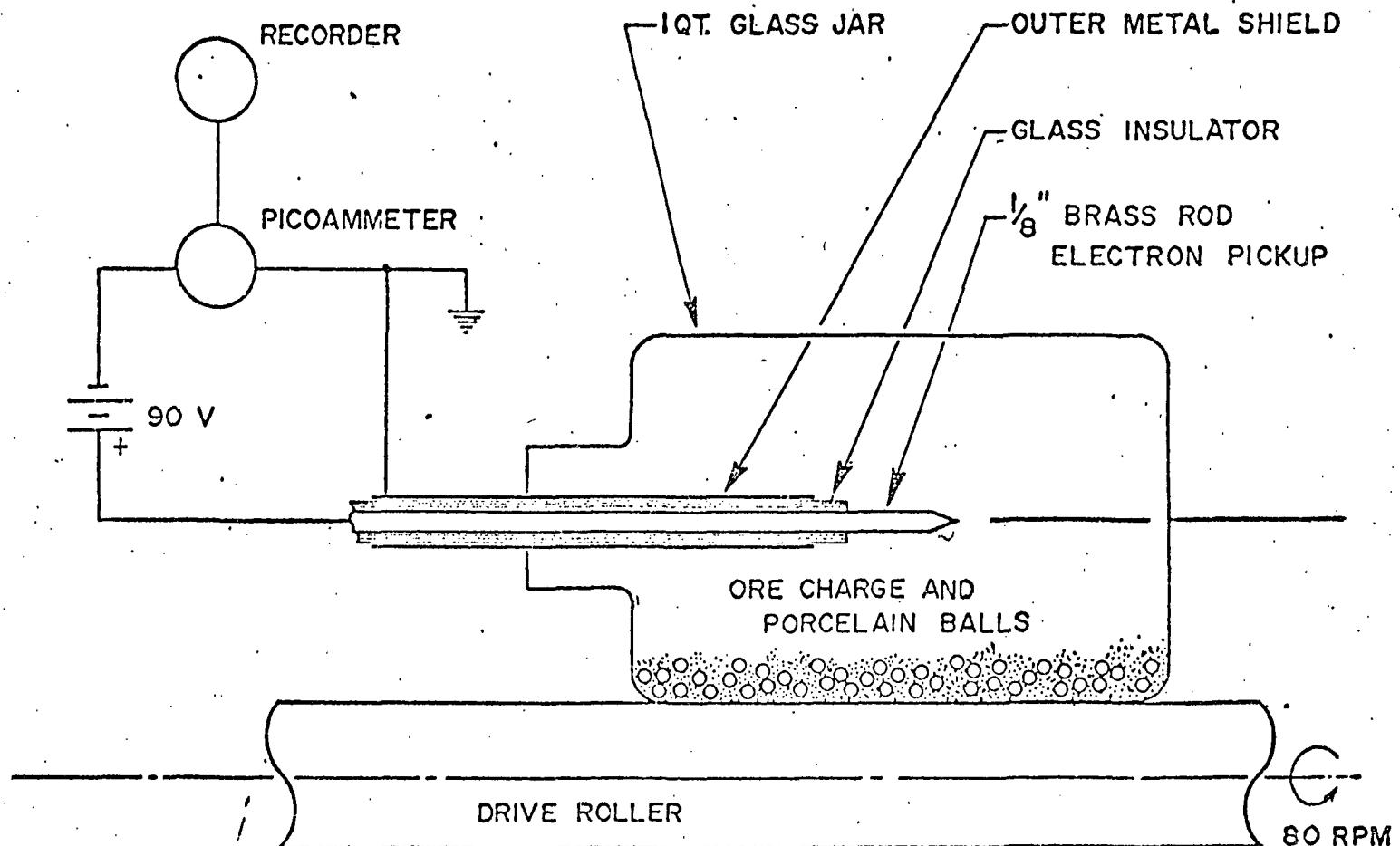
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EXO-ELECTRON GRINDING SYSTEM

Figure 1

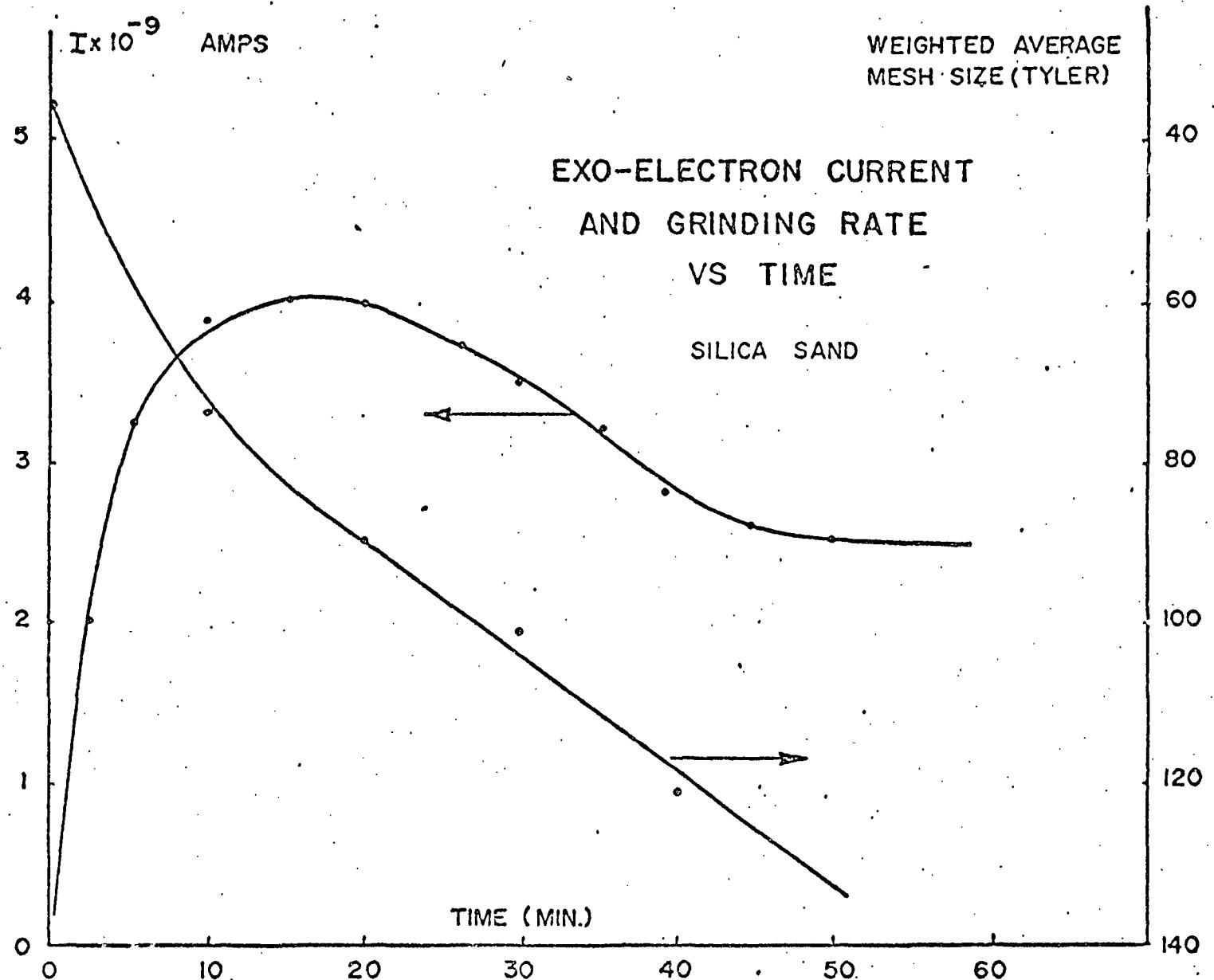


Figure 2

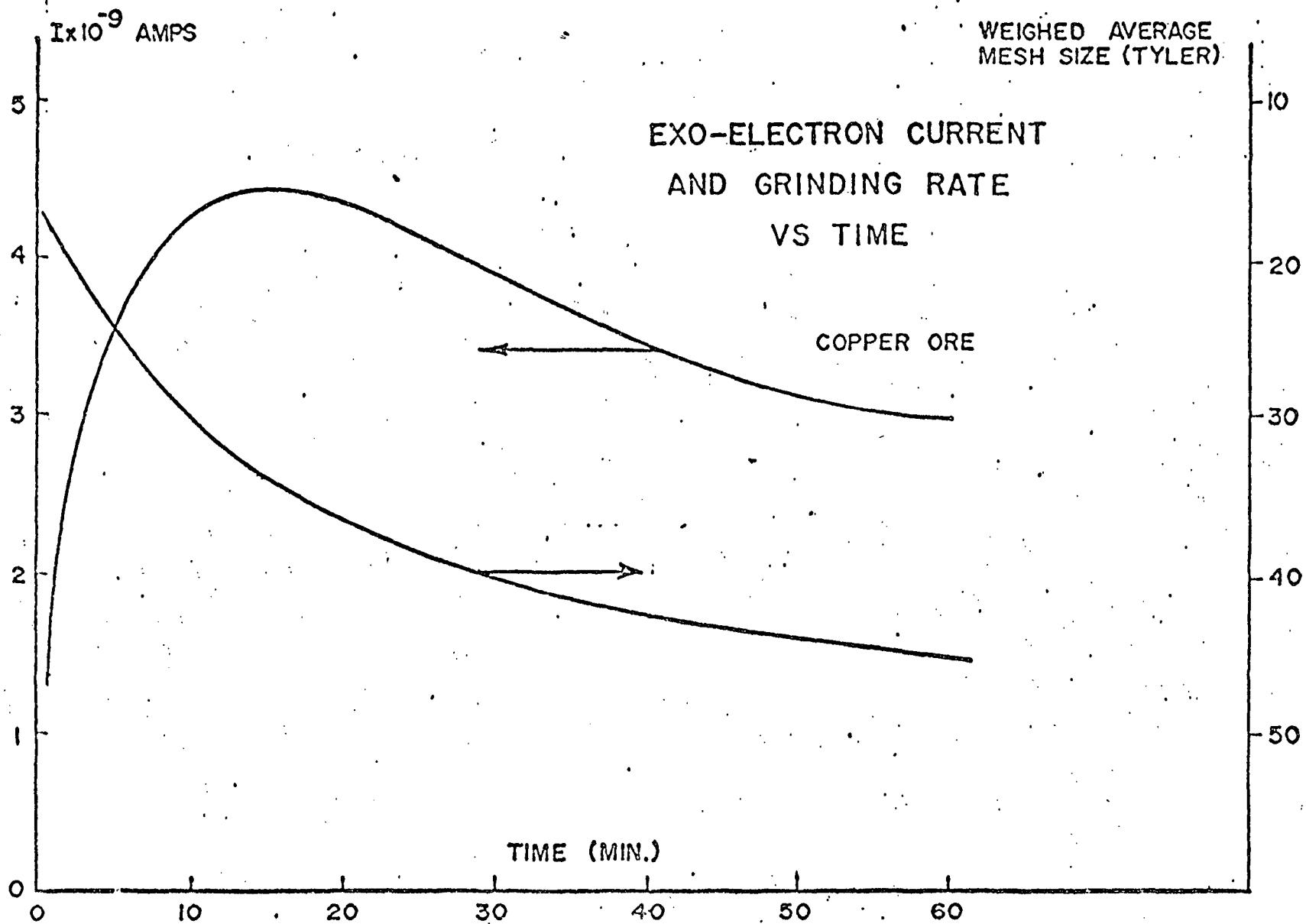
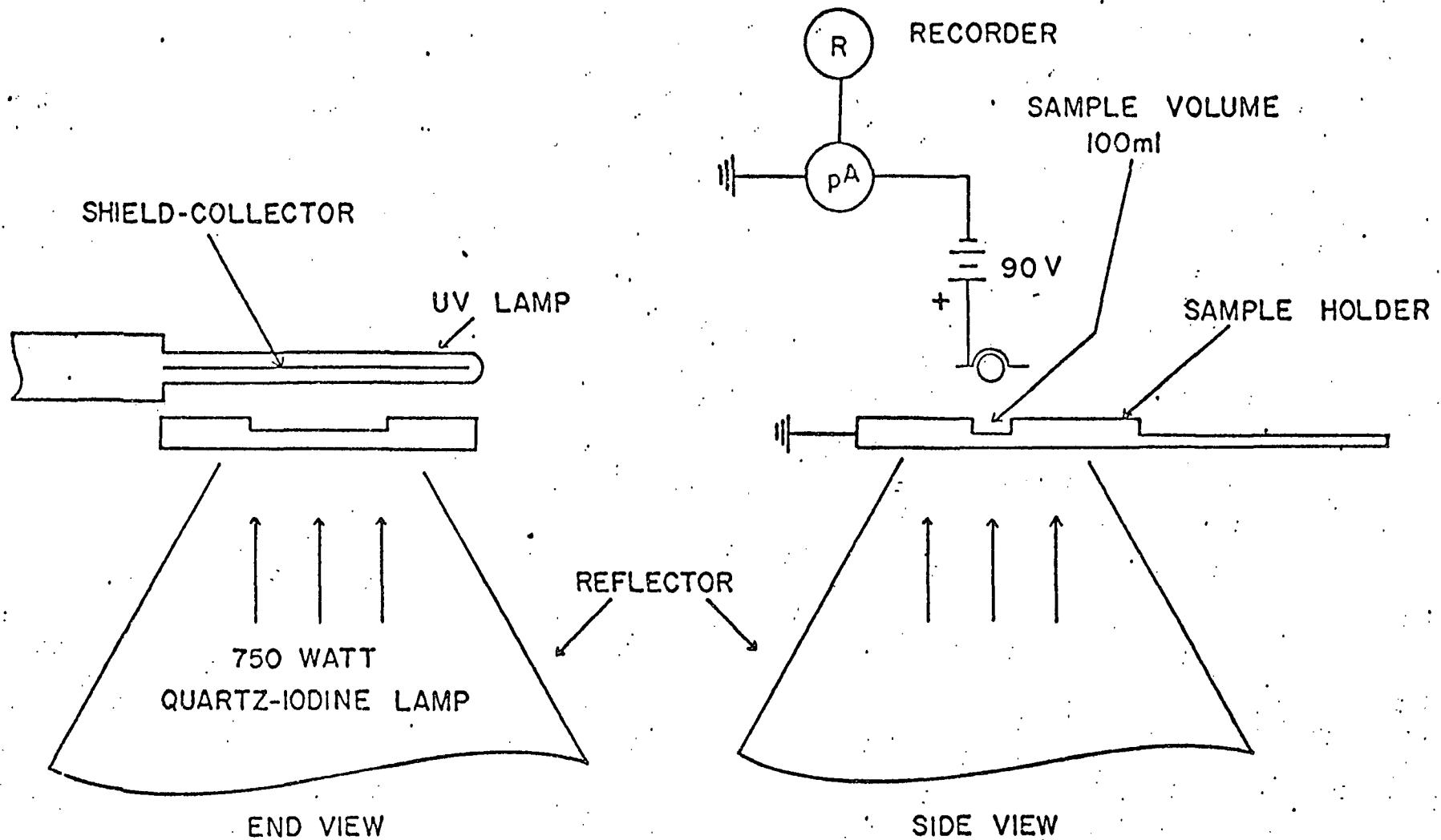


Figure 3



EXO-ELECTRON POWDER TEST SYSTEM (SCALE NONE)

Figure 4

SPECIMEN	% FREE SILICA
SHALE	56.23
SLATE	32.46
GRANITE	29.32
FOUND. DUST	25.39
TRAP ROCK	3.33
CLAY	26.40
SILICA BEADS	98.00

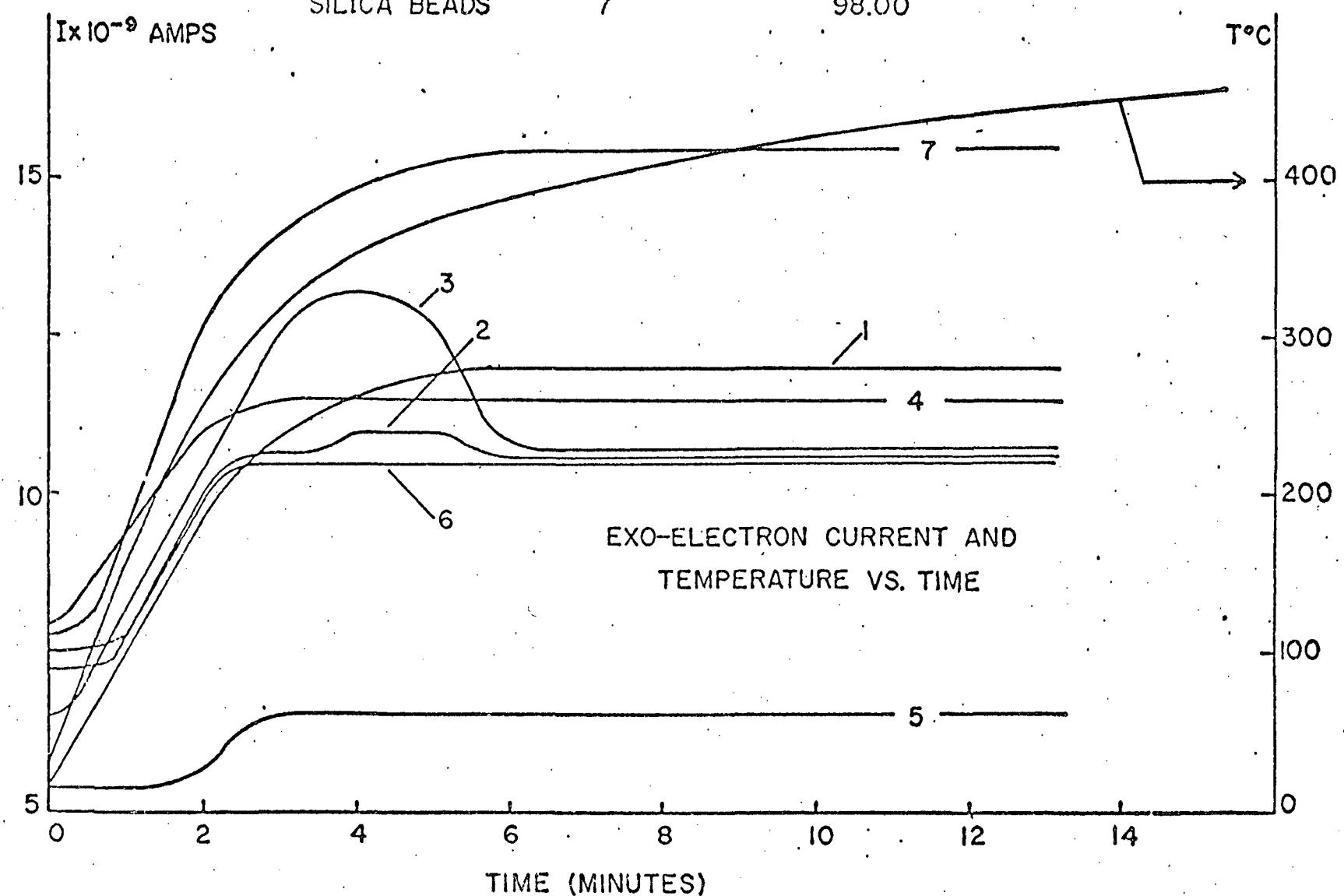
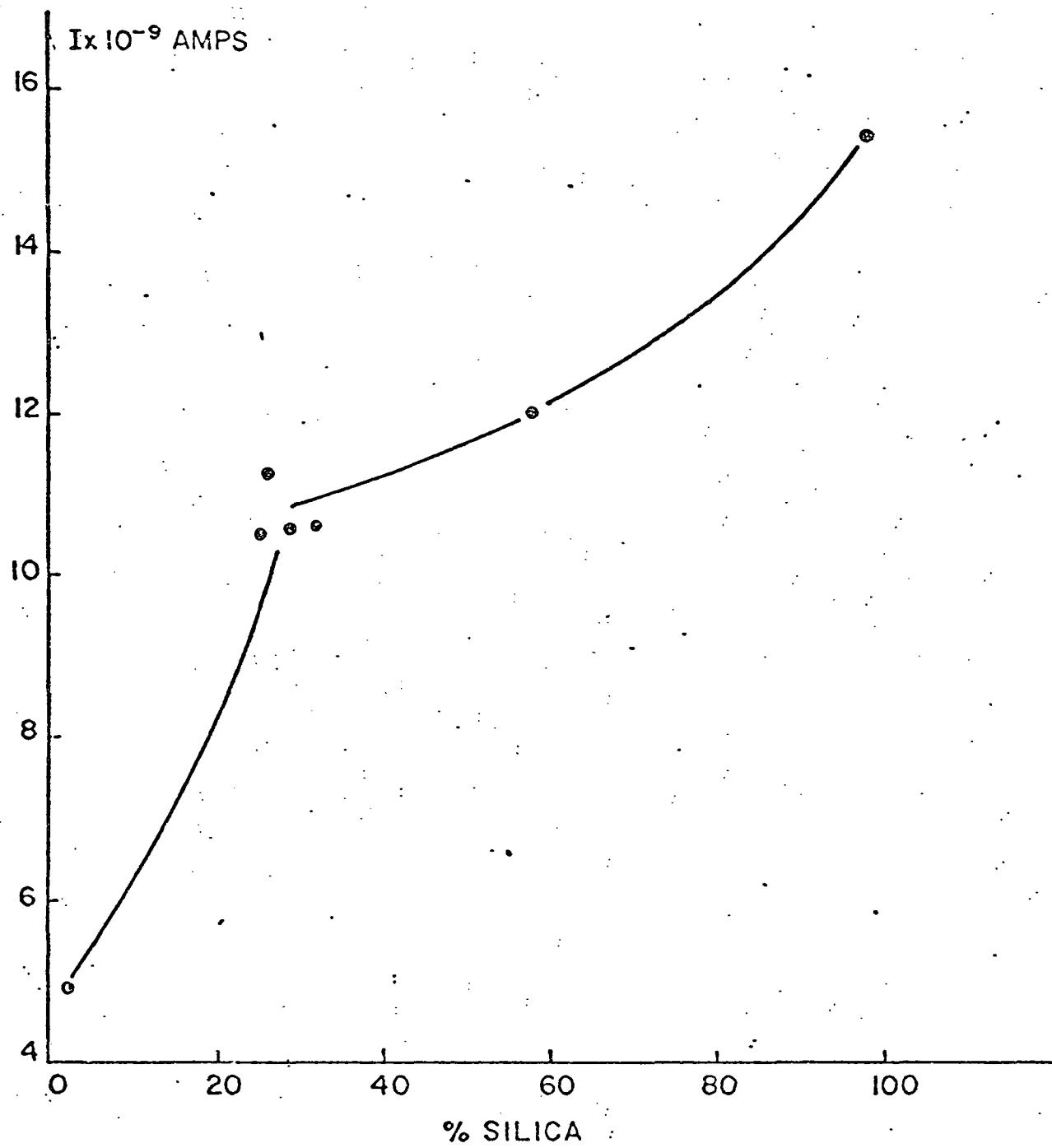


Figure 5



EXO-ELECTRON CURRENT LEVEL AFTER 8 MINUTES  
VS. SILICA CONTENT

Figure 6

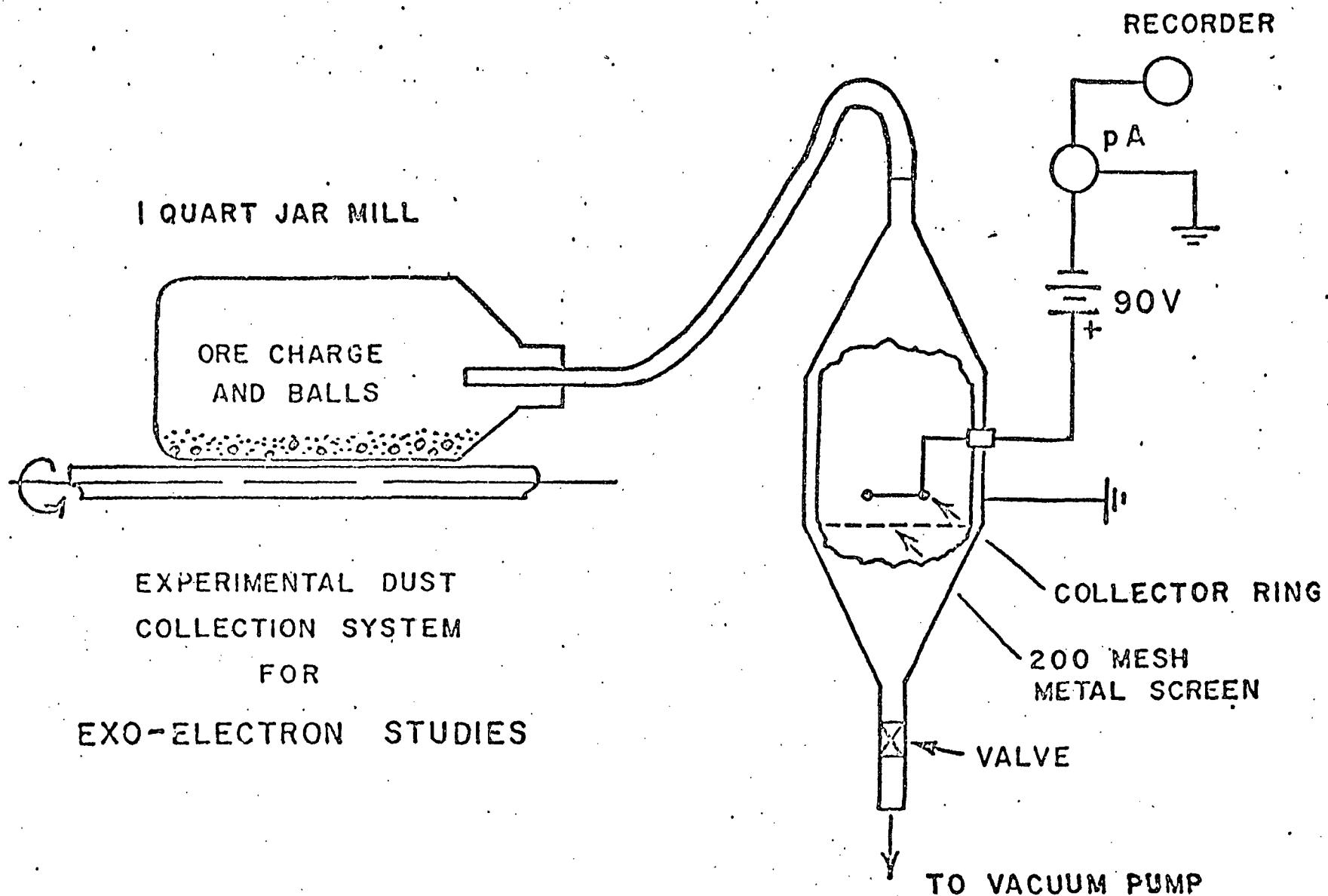


Figure 7

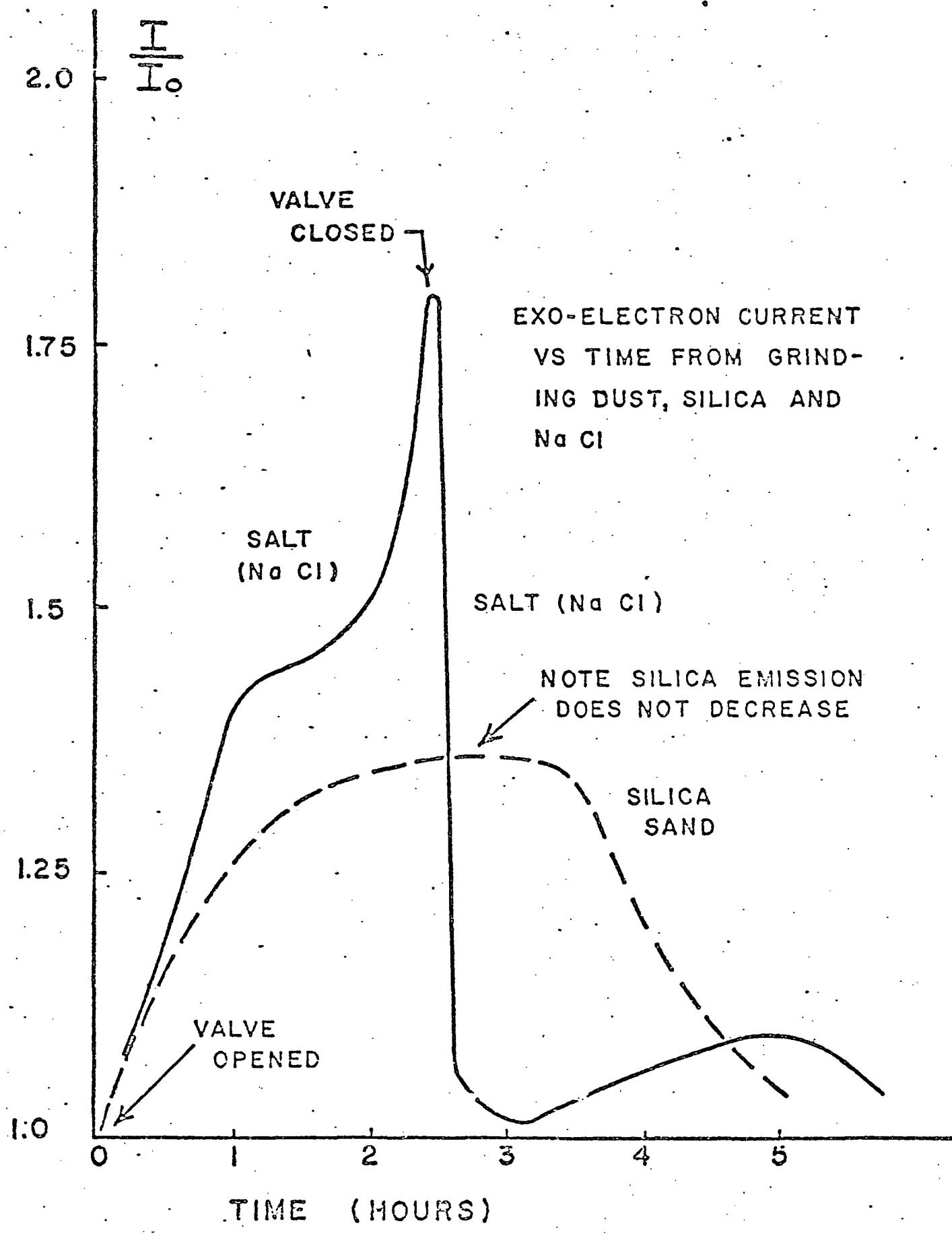


Figure 8

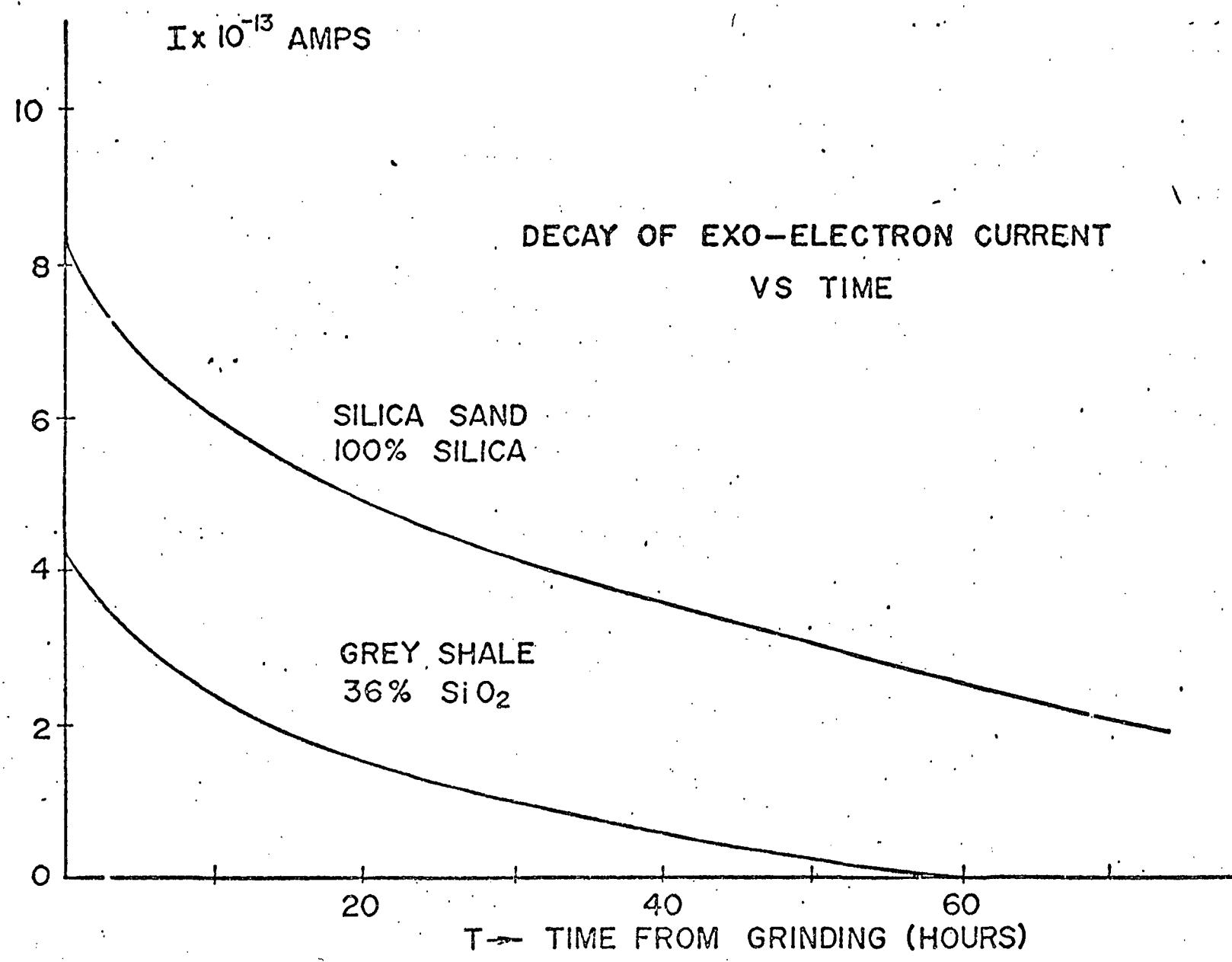


Figure 9

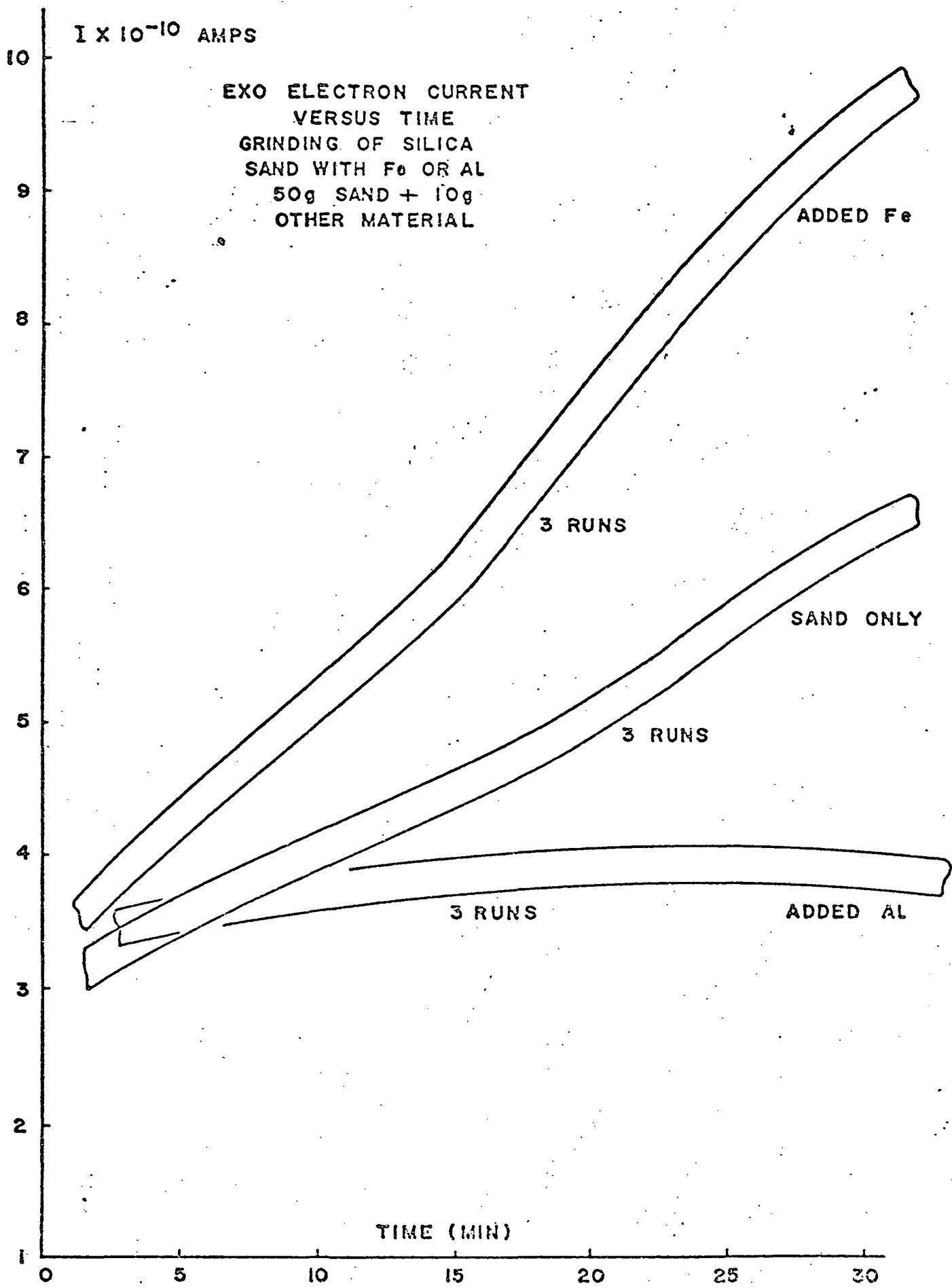
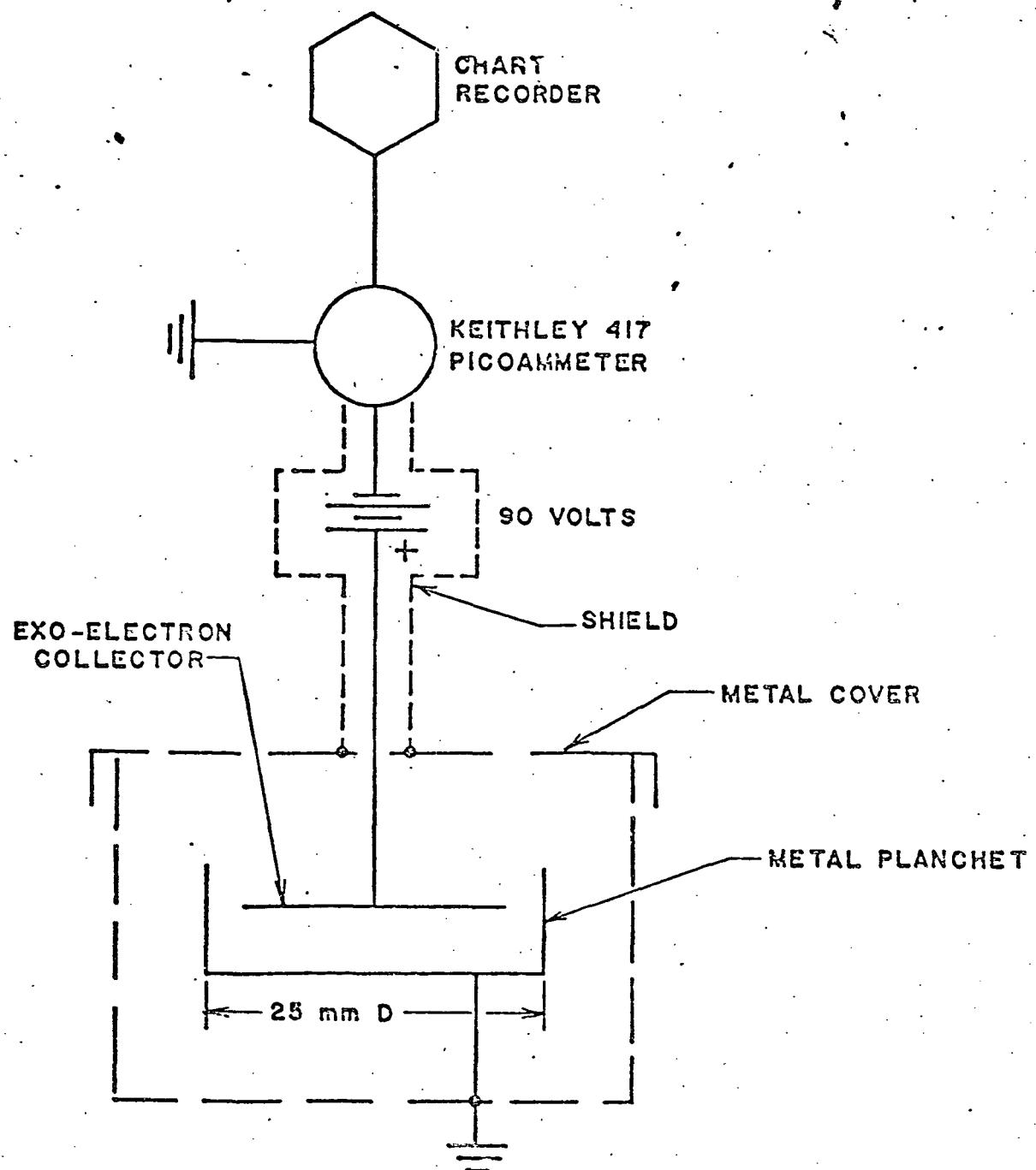


Figure 10



EXO-ELECTRON DETECTOR SYSTEM

Figure 11

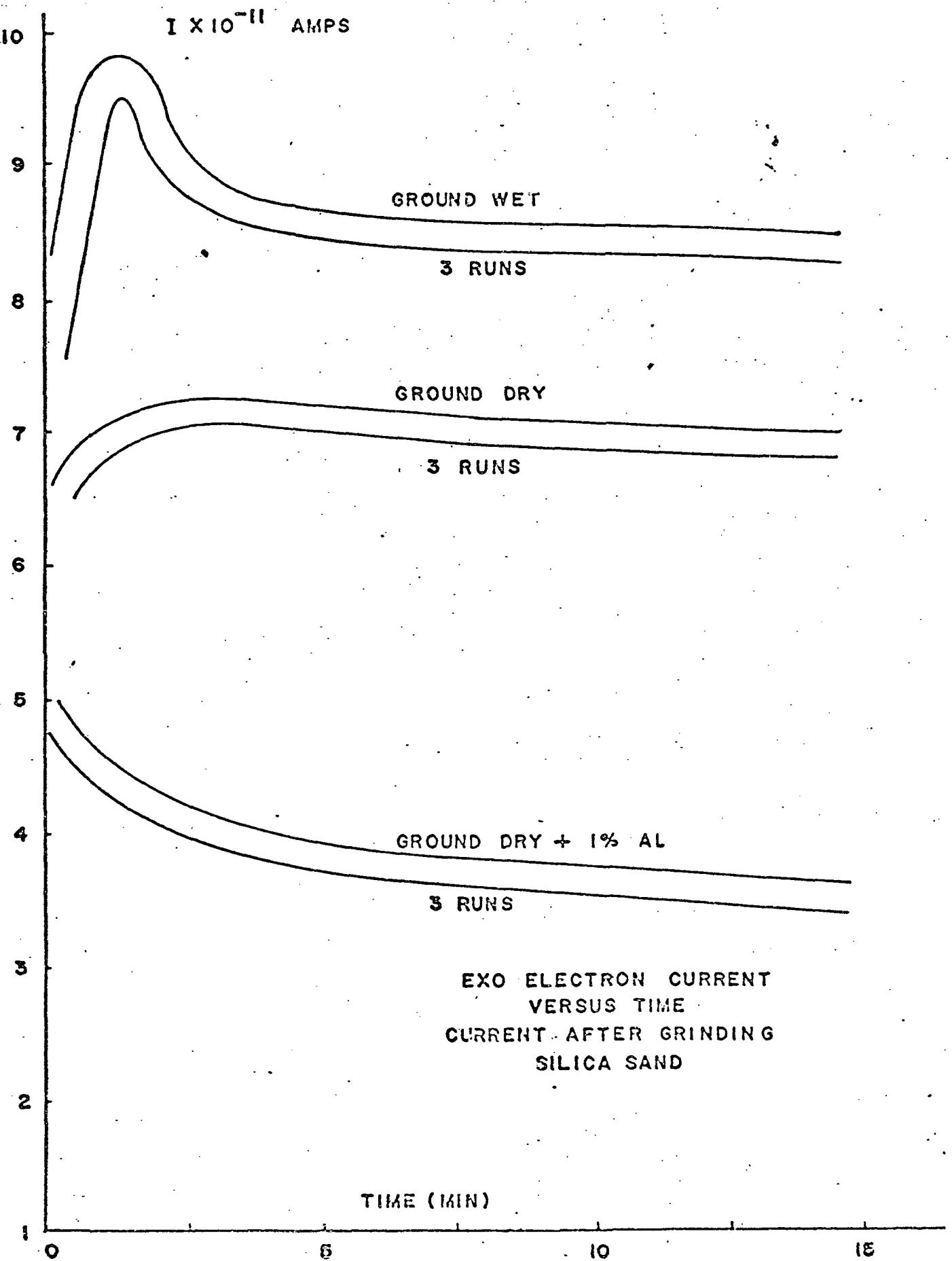


Figure 12

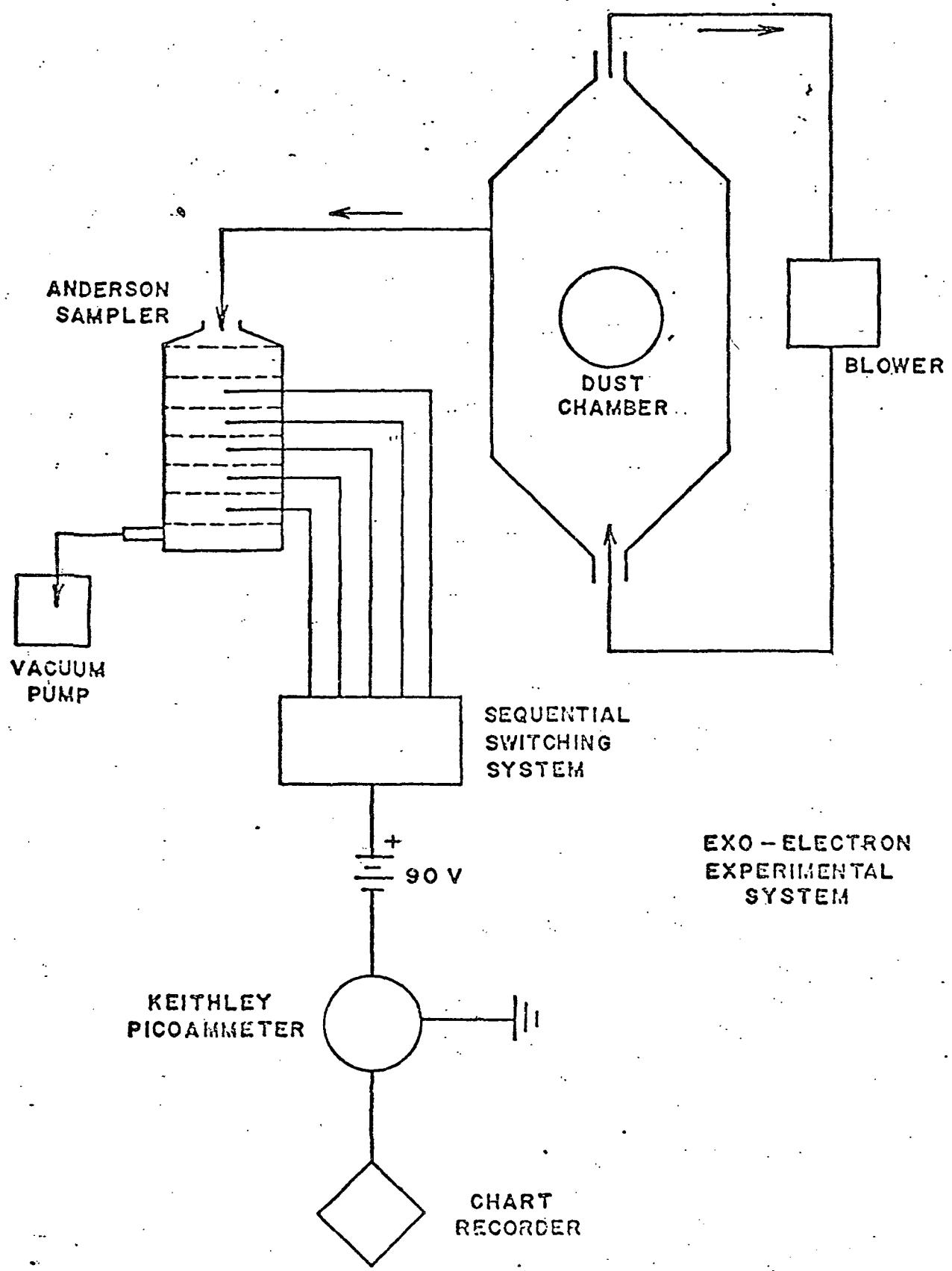
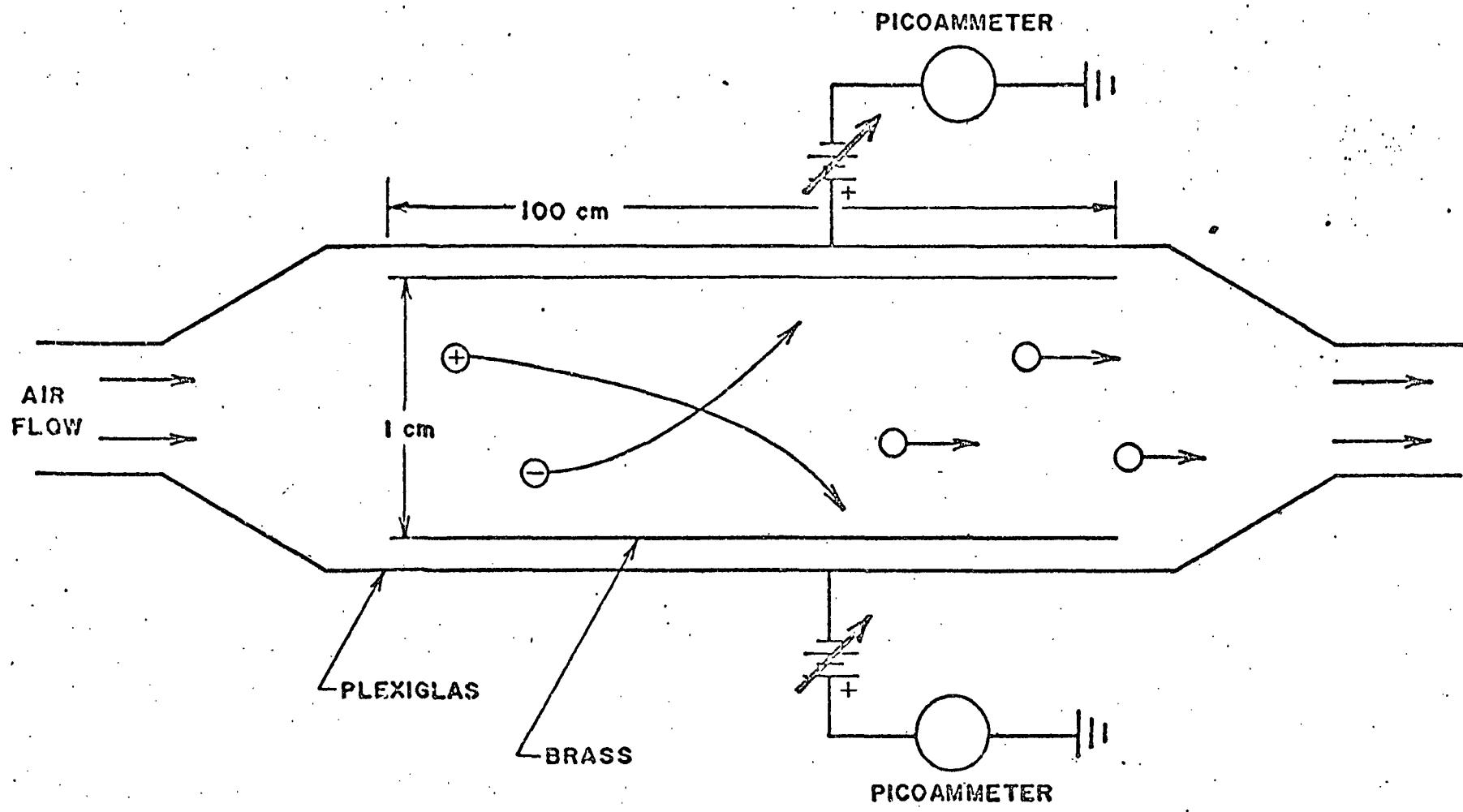
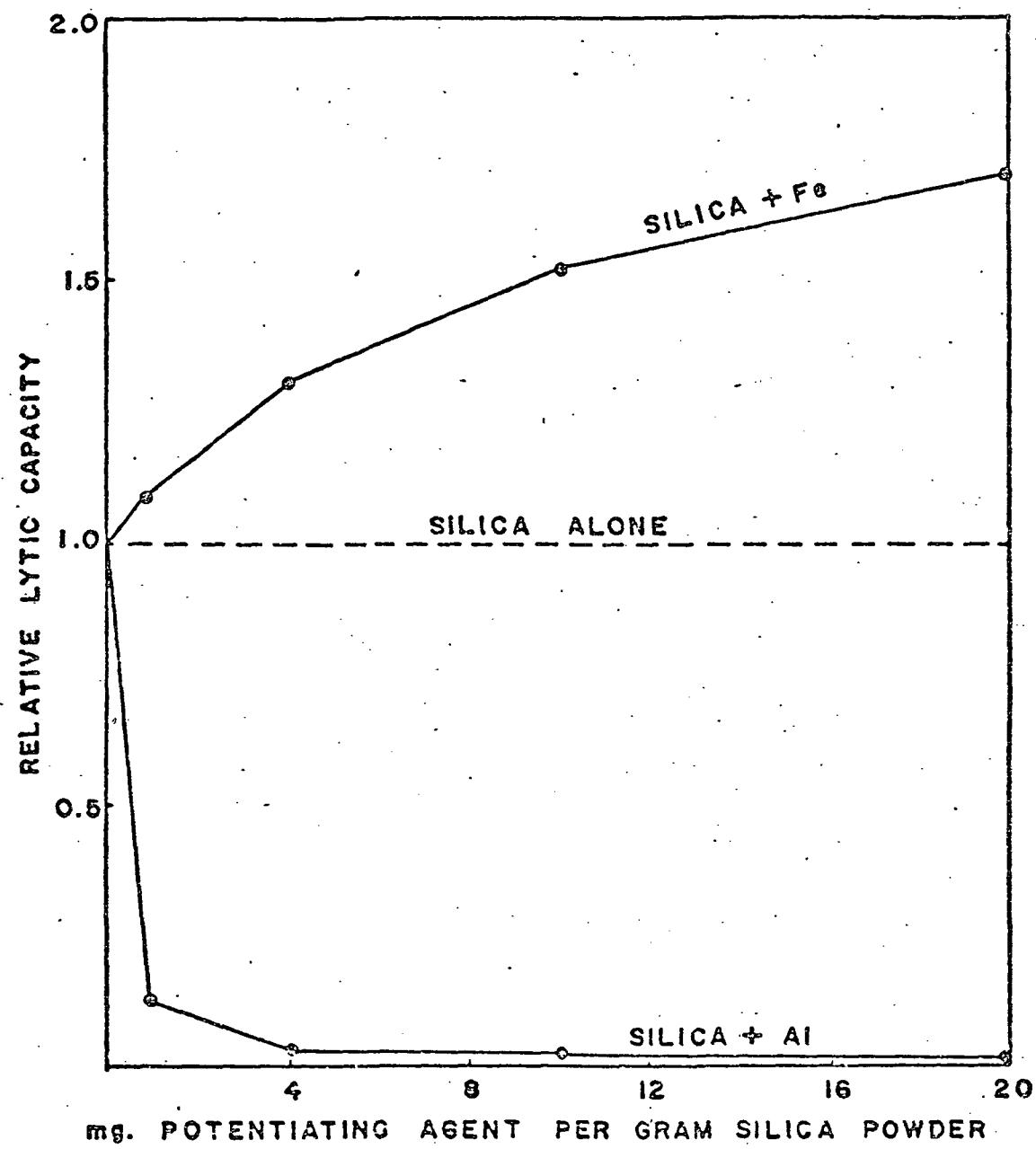


Figure 13



CHARGE SAMPLER

Figure 14



EFFECT OF IRON AND ALUMINUM  
ON THE LYTIC CAPACITY OF SILICA

FIGURE 15

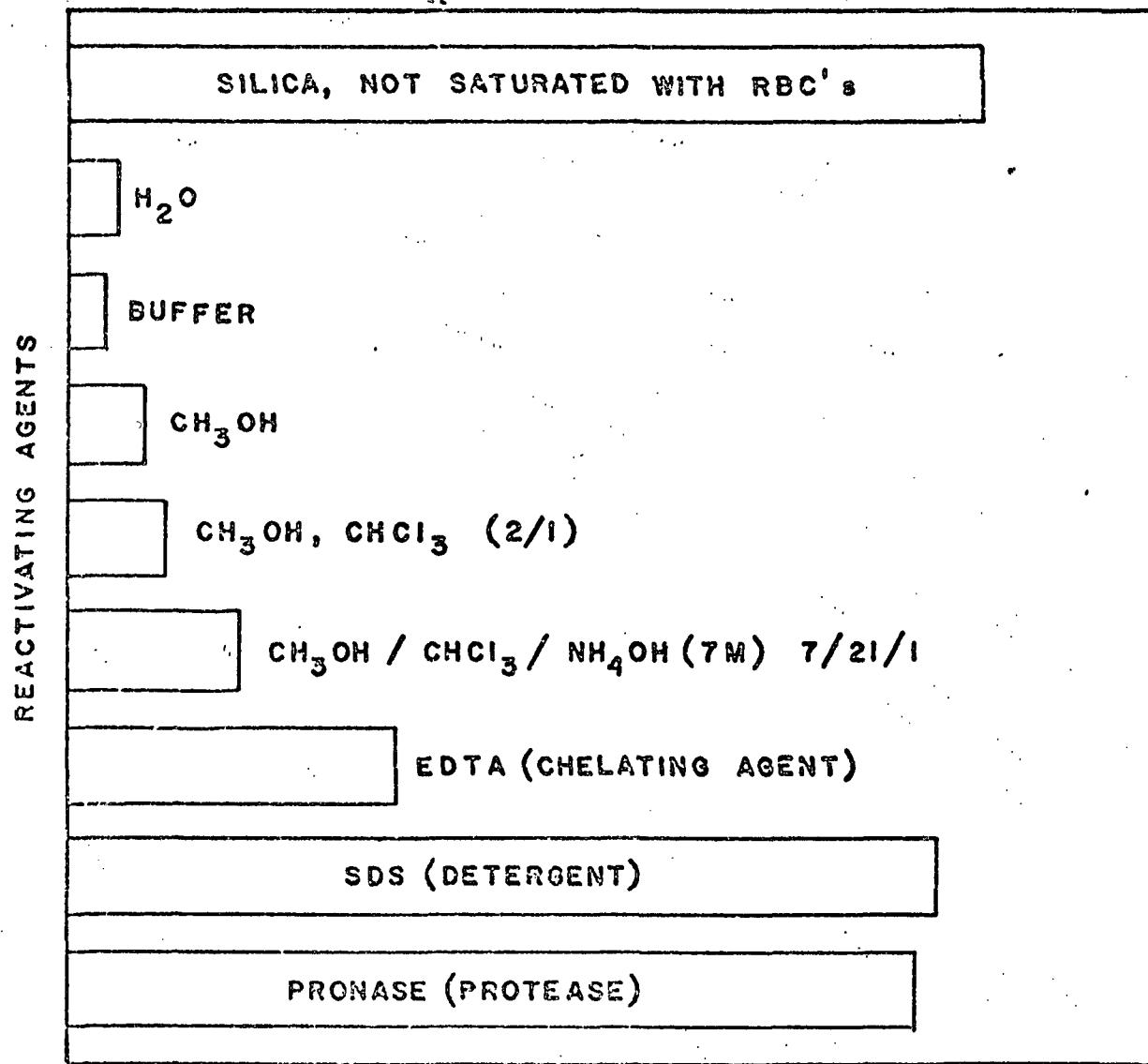


FIGURE 16  
RELATIVE LYtic CAPACITY OF REACTIVATED SILICA

APPENDIX B

NON-DESTRUCTIVE EVALUATION OF FATIGUE, GRINDING  
AND CATALYSIS BY MEANS OF EXCELECTRON EMISSION

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### Introduction.

The term exoelectron emission (EEE) is generally used to designate any electron emission that does not fall into the usual thermal, field or secondary emission characteristics. As such we must recognize that EEE can be induced by a variety of external phenomena ranging from plastic deformation to X-rays and corrosion-oxidation processes (1). The application of EEE to non-destructive testing is predicated upon the assumption that it is possible to separate the EEE signal from fatigue, crack formation, annealing, grinding or catalysis, from interferences due to dirt, paint, scratches, oxidation, ionization or leakage.

In this paper we shall focus attention on applications of EEE to practical applications in the field of NDT. This is not to denigrate the importance of basic studies of the process of EEE itself; we are all aware of the need for a complete understanding of why materials emit exoelectrons. It is rather a case that we at the University of Arizona have chosen to devote our efforts to developing ad hoc applications of the EEE phenomena to industrial processes.

In earlier publications (2, 3) we have reported on the measurement of EEE from metals and non-metals. Most of these studies were done in ambient air to simulate the actual situation in an industrial plant. In spite of the constraints imposed by the environment, it was possible to observe EEE as coupons were fatigued and to predict the point of eventual failure. Some experiments on post-fatigue EEE were done to evaluate the technique for measurement of damage in structures at various points during their working life.

These post-fatigue EEE studies required that the specimen be heated to some 90°C and this appeared to be a definite limitation to the

application of EEE. Another pertinent objection to the work of references 2 and 3 was the concentration of effort on rather ductile metals and low-cycle-high-stress fatigue testing. If, as was suggested, the EEE phenomena required significant plastic deformation, this would preclude its application to high strength materials with low ductility.

Since the last publication there have been more extensive studies of the EEE phenomena on high-strength metals at room temperature and it appears that some of the objections to the earlier work can in fact be removed. Many questions still remain, in particular the actual driving effect that induces EEE.

#### The Induction of Exoelectron Emission.

We propose to discuss our experimental work in terms of a model involving the diffusion of vacancies to the specimen surface as the driving force for EEE. Here we hasten to add that this mechanism is not generally accepted by workers in the field and we use it only as a conceptual model. However wrong it may be in detail, it provides (in our opinion) the best correlation of the experimental observations. It is presented as a correlation model without analytical justification.

In this connection we should indicate what is actually measured when experiments are performed in ambient air. If an electron is emitted into air at one atmosphere, it is almost immediately captured by an oxygen molecule to produce an oxygen negative molecule ion. These ions are drawn to a positive collector and provide the current that we measure. The term exoelectron current will be used with the understanding that in air the current is really oxygen negative molecular ions.

### Experimental Studies of Fatigue and Fracture

We have looked at a great variety of experimental systems without attempting to carry the studies in any one area into great detail. This was done deliberately with the idea that it was important to define the areas where EEE could be applied before studying any one application at length. In many of these areas work is still going on and this paper will present the results and conclusions to date.

We will discuss the fatigue-fracture-annealing studies in some detail. A short discussion of the applications of EEE to grinding, catalytic studies, and industrial health will be given at the end of the paper.

The apparatus used for most of the tests was a modified Detroit Testing Machine Company hydraulic fatigue system. Tensile loads up to 4,000 lbs. could be applied at a cycle rate of 2 cps. We had no provision for measuring strain, the system simply raised the load to some preset value and then dropped it to zero ( $R = 0$ ).

The EEE detector scanned along the specimen coupon at a rate of one inch per minute; the testing machine and scanner are shown schematically in figure 1. The detector and the electrical system are shown in more detail in figure 2. The typical coupon shape is shown in figure 3.

#### I A Coupons With Drilled or Tapped Holes.

Many industrial structures have a variety of drilled or tapped holes which may or may not be filled with screws or rivets. These holes are often the site where fatigue failure begins and it is of interest to

determine the capability of EEE to predict the site of final failure. For this experiment the aluminum 7075-T6 coupon was drilled with 4 holes 1/8" diameter spaced 5/8" apart. The coupon was cycled in tension and the scanner moved back and forth to cover the holes one by one. Typical results are shown in figure 4. It is clear that the hole at which failure would occur could have been predicted quite early in the fatigue cycle.

Similar data on aluminum 2024-T81 is shown in figure 5. The emission from the hole at which failure finally occurred (No. 4) is larger than that from a typical other hole (No. 1). The surges in EEE current marked on figure 5 are often observed in our experiments and may be associated with the formation and growth of cracks. Such surges are usually an indication of impending failure and as such are of great interest to us. More data on this topic will be reported below.

#### I B Ccoupons With Filled Holes.

For this experiment the 2024-T81 coupons were drilled as before and the four holes were filled by installing 2-56 steel machine screws (countersunk). In this case the machine screws were not exposed to any load during the fatigue test, they were simply installed to fill the drilled holes. The coupon was fatigued and scanned in the usual way, typical results of a number of experiments are shown in figures 6 and 7. The two figures differ somewhat in detail, but there is no question about the ability of the EEE system for prediction of the point of eventual failure. In one case (figure 6) one surge in the EEE current from the screw, at which final failure occurred, can be observed. In the other figure 7 the EEE from the screw at which final failure occurred was always higher than that from a typical "normal screw" which we have shown as the other curve in the figure.

### I C Bolted Structures.

For this study the assembly shown in figure 8 was made up of pieces of broken 2024 - T81 specimens. The bolts were 10-32 cadmium-plated steel with brazier heads. They were tightened to the recommended maximum torque and the assembly was fatigued by applying a tensile load.

We recognized that with this assembly the tension load would induce some bending moment, but we felt that the resultant lateral motion during the fatigue process would be a good test for the application of EEE in industrial situations. The results are shown in figure 8 and once again we note that the point of eventual failure could have been predicted early in the fatigue cycle. Two surges in the EEE from screw No. 2 were observed. The signal received from screw No. 1 at the same time may have been due to electrons emitted by screw No. 2 and drawn to the electron collector when it was positioned over screw No. 1. This lack of spacial resolution is due primarily to the capture and scattering of oxygen molecular ions by ambient air molecules. It may be partially compensated by improved probe design but the resolution in air will never approach that in vacuum.

It appears that the EEE system can be used for testing systems with holes, filled holes or bolted structures. We must caution, however, that these latter effects may be limited to aluminum where failure in bolted systems involves fretting. Examination of the bolted systems after failure indicated significant fretting which may not occur with other materials. Studies of bolted systems with other materials are under way.

## II Studies of Slotted Coupons.

We began this study with titanium after exploratory work indicated that detection of fatigue and cracking in Ti coupons with holes would be very difficult. The problem originates in the tendency for Ti coupons to crack inside a hole with little or no indication of damage outside the hole. If the holes are large enough (about 0.100"), an EEE probe can be inserted into the hole itself for detection of exoelectrons but the lateral motion in our test system rendered this technique impractical. We tried drilling larger holes but the test coupons were so erratic in their life three cycles that the attempt was abandoned and we chose to mill<sup>1/4</sup> slots across the face of the coupon to induce failure at one of three locations.

The Ti used for these studies was the 6Al-4V alloy, three slots 0.020" deep and 0.015" wide were cut on a milling machine; the coupons were washed and air-dried before testing. The coupons were fatigued in tension and the slots were scanned with the EEE detector system. Typical results are shown in figure 9 along with a typical scan. The emission from the three slots varied greatly from slot to slot because of inescapable differences in machining. For this reason we took the initial peak height for each slot before fatiguing and called this the base level  $H_0$ . The emission from each slot during the fatigue process was divided by the appropriate value of  $H_0$  and plotted as  $H/H_0$  for the three slots. This data is shown in figure 9 and it is clear that the eventual failure at slot number 3 could have been predicted at an early point in the fatigue cycle. Other data of this type on Ti-6Al-4V is shown in figure 10. Here the load was reduced and the experiment extended over a two-day period. It is interesting to note that during the night the fatigued specimen

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remained for 18 hours at no-load but the EEE observed the next morning (without additional cycling) was larger than that observed when the experiment had been stopped the previous evening. This increase in EEE observed under no-load conditions was always noted with this material. Following our exoelectron-vacancy theory we suggest that during the fatigue cycle the diffusion of vacancies to the surface is impeded by fatigue-induced structural defects. Under no-load conditions the vacancies have time to diffuse to the surface and THEN release exoelectrons when illuminated by the UV light. We shall present more data to substantiate this suggestion below.

The results of another test on a slotted Ti coupon are shown in figure 11. Here the coupon was allowed to "age" in the laboratory for a week after the slots were cut. We hoped that the excess EEE from machining operation would have a chance to decay and the normalization technique used for figures 9 and 10 would not be needed. There was some decay but the normalization technique was required to reduce the data. The results, including a typical scan, are shown in figure 11. The slot where failure finally occurred (No. 1) showed an excess of EEE after some one third of the specimen life had been achieved. The emission from all three slots decayed as fatiguing continued, but when the specimen was left at zero load over night, the emission from all three slots increased. When the fatigue machine was started again, the emission from all three slots decreased as before, but the current level of slot 1 remained above that of slots 2 and 3.

In all three cases the broken coupon was subjected to microscopic examination at 200X for evidence of extensive slip before failure. No such evidence was observed suggesting that there is no requirement for extensive slip to induce exoelectron emission.

### III Studies of Coupons without Slots or Holes.

In our earlier experiments, reference 3, we demonstrated that the fatigue level and point of ultimate failure could be measured on coupons without slots or holes. Typical data of this type, taken from reference 3 is shown in figure 12. To obtain this data the coupons were first fatigued to some fraction of their total life and then heated to 90°C with an induction system that scanned along the coupon. This requirement that the coupon be heated was a severe penalty to the application of EEE for post-fatigue evaluation studies.

Recently we have again approached the problem of predicting the location of final fatigue failure on a coupon without notches or holes to induce failure at one or more pre-chosen locations. For this study the first material was pH14-8Mo steel heat-treated into the SRH-1050 condition. This was by far the most brittle material that we had available and was thought to serve as a test of the EEE under severe conditions. The data taken during the fatigue test is shown in figure 13. Periodically during the run we stopped the fatigue cycling and scanned the coupon under zero load conditions without heating. This zero load data did not differ from that taken during the fatigue process itself and is not shown in figure 13. The significant feature of figure 13 is the substantial drop in EEE level in the area where final failure occurred. In this case, the minimum in the EEE current was observed at some 53 mm along the coupon while the actual point of failure was at the 73 mm location. This may have been due to exoelectron emission from the point where the grips contacted the specimen at the 90 mm point. [This lateral flow of electronic charge from one location to the probe when it is at a nearby point

is a problem which we hope to relieve by using a series of fixed probes and sequencing the signals from the various probes into the detector.] More data on this material is shown in figure 14. Here we have plotted the EEE current with respect to a base line for the point where failure finally occurred as a function of the number of cycles. Again we notice that after an initial surge the emission drops continuously until some 75 per cent of life at which time it begins to rise again. This type of behavior seems to be characteristic of the high strength materials and we suggest that in the area where fatigue damage is most intense the exoelectron emission will drop to its lowest level because this damage impedes the migration of dislocations to the surface of the coupon.

Similar results are shown in the next figure 15 where the material was in the annealed condition. Here the EEE drops with fatigue cycling, rises during the night under no load conditions, and then decreases again as cycling resumes. An increase in emission is observed as a crack forms and the material fails. The general level of EEE is higher with this annealed specimen and we suggest that this is due to the increased rate of vacancy migration in the softer material.

Other data on the pH14-8Mo steel is shown in figure 16 where we have traced a series of scans at different times during the fatigue cycle. The point at which failure finally occurred is shown as a vertical line. The interesting thing about this data is the way that the curves change shape during the test. Initially there are large peaks and valleys due, no doubt, to variations in surface condition. As cycling proceeds ~~THE AREA~~ at 76 mm begins to decrease its level of EEE while in other areas the peak-to-valley distance is reduced as

the emission from the valley areas begins to increase. This is particularly apparent in the 70,000 cycle trace where the 76 mm valley level is some 2-1/2 times lower than the level of the rest of that particular trace. As cycling continues the valley is still apparent but it is not as prominent as it was at 70,000 cycles. It is interesting to note that the valley at 55 mm, so apparent at 30,000 cycles, has almost disappeared at the 140,000 cycles point. This makes the valley near 76 mm more apparent and allows us to predict the approximate location of the failure point. We notice that the vertical line does not always pass through the lowest valley point. We have no explanation for this at the moment and suggest that the appearance of a low point in the EEE permits only the approximate (within  $\pm 5$  mm) location of the point of failure.

We suggest that for the pH14-8Mo material the decrease of EEE signal from a particular area can be used for prediction of the approximate location of final failure.

Similar data for 2024-T81 aluminum is shown in figure 17. In this case coupons without holes or slots were fatigued at the Rockwell International Los Angeles facility to some fraction of their expected life (typically 5 million cycles). The coupons were shipped to the University of Arizona and scanned for exoelectron emission without heating. The coupons were then returned to RI and cycled to failure. The number of cycles to failure and the point at which failure occurred was transmitted to the U. of A. In figure 17 we show first a typical scan taken before failure with the point of final

failure marked. The current level "Y" was measured for every coupon from the tracing taken before failure and in figure 17 we have plotted the values of "Y" versus the fraction of coupon life that had been expended when the trace was taken. While the number of data points is limited, there seems to be some significant information. Initially the EEE level rises with fatigue and then it begins to drop until almost the end of life at which time it begins to rise again. This data might be compared to that of figures 13, 14, 15, and 16 where we reported that the EEE level declined during the fatigue process and the decline was most pronounced at the point where failure would be expected to occur.

Again we suggest that this drop in EEE level is due to the build-up of fatigue damage interfering with the flow of vacancies to the surface of the coupon. This interpretation is our own and should not be taken as that of Rockwell International Corp. or its employees.

#### IV Crack Growth Studies.

Efforts to apply the EEE technique to the growth of fatigue cracks was an early objective in our program. The primary difficulty has been developing an experimental arrangement that will allow the growth of fatigue cracks in a controlled way. Earlier experiments, references 2 and 3, involved the controlled tearing of a material with a system built around an automobile jack. In those studies significant EEE currents were observed and the growth of fatigue cracks has been an important area of investigation. Recent studies have made use of a ductile material (strap iron, a hot-rolled low carbon steel) in order to stop a crack with our simple test system. Attempts to stop cracks in harder materials, i.e. aluminum 7075-T6 and Ti-6Al-4V were unsuccessful, as soon as a crack formed the material failed.

Typical results with the strap iron coupons are shown in figure 18. The coupon was a strip 1" wide by 0.103" thick with a 0.050" or 0.100" deep notch cut on one side. The load was kept at 1500 lbs throughout the test. For the first 57,000 cycles no crack was visible and there was no visible plastic deformation, but a groove formed in the area where the crack was expected to appear. When the first crack appeared there was a significant increase in EEE. This initial level of emission declined as further crack growth relieved the built-up stress. Periodically, further crack growth was observed and each increment of growth was signaled by a surge in EEE. During the night the coupon was kept under no-load conditions and the emission decayed. When cycling was resumed the crack began to grow almost immediately and this growth was signaled as a series of surges in the EEE current. The experiment was stopped when the crack grew too large to measure with the reticule in our microscope.

Other data of this type is shown in figure 19. Here the initial load was lowered to 750 lbs and extensive plastic deformation, without the inception of a crack, was observed for some 12,000 cycles. During this period the EEE detector was scanned away from the notch to see if the EEE from the notch area had already begun to be larger than the emission from the rest of the coupon. This was definitely the case and is an indication of the ability of the EEE technique to detect areas where crack formation will occur. At some 12,000 cycles the load was increased to 2,000 lbs and cycling continued to 18,000 cycles where the load was raised to 3,000 lbs. At this point a crack or what we took to be a crack appeared but no change in the EEE level was observed. [We suspect that in this case the crack did not extend entirely through the coupon. With

the EEE detector on one side of the coupon and the microscope on the other we must expect occasional differences of this type.] Some 50 cycles later a large crack 0.020" long appeared and was observed to penetrate entirely through the coupon. The appearance of this crack was signaled by a very large drop in EEE, then as the crack continued to grow, the emission level rose rapidly until the coupon failed.

It is interesting to note that in one case when the first crack appeared the EEE level rose while in the other case the EEE level fell when the first crack was observed. We have noted this effect a number of times and suggest that it is due to the level of gross plastic deformation in the coupon before the crack appears. If there has been extensive plastic deformation before a crack appears, the appearance of a crack is signaled by a decrease in EEE. Conversely, if little or no plastic deformation has occurred before a crack appears, the event is signaled by a substantial increase in EEE level. We suggest that in the first case most of the stresses are relieved by the plastic flow and the first crack relieves whatever stress remains, thereby decreasing the observed EEE. If very little plastic flow has occurred, the first crack represents a gross movement of dislocations and as such generates a substantial EEE current. Effects of this type can be observed in figures 18 and 19. In the latter stages of crack growth, very little plastic deformation is taking place and each increment of crack growth generates a surge of EEE.

#### V Annealing Experiments.

Annealing studies have been a small but important part of our EEE work for two reasons: first, they represent a significant application of the technique to a variety of industrial problems. Second, they may be an important factor in the final explanation of the how and why of the whole EEE process.

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Our first studies in this area were done with highly purified platinum wire quenched in liquid nitrogen and then annealed in an isochronal cycle. The results were reported in detail in reference 3. Here we shall only reproduce one of the figures as figure 20. As the wire was annealed, we observed the EEE as a function of time through each of the steps in the isochronal cycle. The observed current increments ( $\Delta I$ ) are plotted in figure 20 versus temperature and for comparison purposes we have plotted the data of Schumacher taken by the more conventional technique of resistance measurement (Reference 4). There is no question that our data is the first derivative of the data measured by the resistance method. Since the resistance method is known to depend upon the change in the vacancy density during the annealing cycle, we suggest that our data is a measure of the rate at which vacancies are arriving at the surface and being destroyed. This experiment suggests quite strongly that at least in this case EEE is truly dependent upon the migration of vacancies and that this technique offers the opportunity to actually calibrate the system in terms of the number of exoelectrons emitted per vacancy arriving at the surface.

Another study with a direct practical application involved the observation of the annealing of Almen Strips. Almen Strips are used in the evaluation of shot-peening process. Normally the Almen Strip is exposed, on one side only, to the flow of shot and the curvature of the strip is taken as a measure of the intensity of shot-peening. We built an Almen Strip measurement apparatus and exposed strips of standard thickness to a flow of glass shot. The strips were measured to determine their Almen Rating (a higher rating implies a higher level of shot-peening) and annealed in air with a small induction heater. The time-temperature cycle was taken from the published

annealing data for the material involved. The EEE current from the strips was measured during annealing by our usual UV Light and wire pick-up technique. Typical EEE curves versus time are shown in figure 21. Taking the peak value of the emission curve for each strip we have plotted in figure 22 these peak values versus the initial Almen Rating of the strip. There seems to be no question that a correlation exists between the Almen Rating of the strip and the peak EEE observed during the annealing process. This offers the opportunity of measuring the effects of shot-peening directly on the metal part that has been shot-peened rather than getting second hand data via Almen Strips.

Other data on the measurement of shot-peening effects is shown in the next figure 23. Here the material was titanium in the 6Al-4V alloy and our interest was in the ability of the EEE technique to determine when annealing was complete. The metal was shot-blasted and heated by induction to 500°C in air. In figure 23 we show the EEE current from the Ti coupons with and without shot-peening. There is no question that the EEE technique can be used to follow the annealing process. Interestingly enough if a previously annealed specimen is heated again, the EEE current is essentially the same as that from a specimen that had not been shot-peened.

There seems to be no question that EEE can be used for the measurement of the degree of shot-peening of a specimen and for following the annealing-out of the effects of such shot-peening. Since annealing is largely a process where vacancies diffuse to the specimen surface and are annihilated, we suggest that a connection exists between the diffusion of vacancies and the generation of exoelectron emission.

## VI Alloying Experiments.

In another study we observed the EEE during formation of an alloy. The alloying substrate was usually a tungsten filament heated electrically in a vacuum system. Short lengths of wire (Au, Ag, Ni, Cu) were hung on the filament and as the filament was heated the wires were observed to melt and wet the surface of the tungsten. During this alloying process the EEE from the tungsten filament was monitored and related to the strength of the alloy system involved. The details have been reported elsewhere, reference 5. Here we show only figure 24 in which the EEE current is shown as a function of time during the alloying process. A strong alloy reaction, i.e. W/Al, produces a very large EEE current; in contrast a weak alloy system, i.e. W/Ag, produces only slightly more emission than bare tungsten itself.

Here again we comment that alloying involves extensive vacancy motion and that this vacancy motion induces EEE. This suggests again that a correlation exists between vacancy motion and EEE. It also provides an experimental method for studying weak alloy systems.

## VII Experimental Studies At Rockwell International Science Center.

The data reported in this section was taken by Dr. Donald Thompson of the Rockwell International Corporation Science Center. He was kind enough to allow a short discussion of his data at this point. More details and discussion of the apparatus will be reported in the literature. The analysis of these results is entirely that of the authors and should not be taken as that of Dr. Thompson or the Rockwell International Corp.

These experiments were performed in a  $10^{-10}$  torr vacuum system with

provision for argon ion bombardment to clean the specimen. The specimen was fatigued in bending by an electromagnetic driver, the UV light was brought into the chamber via quartz optics. The exoelectron current was monitored with vacuum photomultiplier techniques.

In the first experiments the aluminum sample(1100-0) was cleaned by ion bombardment to remove the oxide layer. An Auger system was used to monitor the decay of the oxygen peak during the bombardment, the complete disappearance of the oxygen peak was taken as evidence that the oxide layer had been removed. Fatigue experiments on the "oxide-free" specimens indicated that there was substantial exoelectron emission suggesting that an oxide layer is not required for EEE to occur.

In other studies the EEE was monitored as oxygen was admitted to the vacuum system. In general the EEE decayed when oxygen was admitted and rose again when the oxygen was pumped off, though the original EEE level was not recovered. Again this suggests that an oxide layer is not required for the emission of exoelectrons; in fact an oxide layer seems to hamper the process.

#### Grinding Experiments and Their Application to Industrial Health.

Our original experiments were devoted to a demonstration that the rate of grinding of industrial materials could be followed by observing the exoelectron current generated during the grinding process itself. The first results of this work have been reported elsewhere (reference 6). Here we show only figure 25 which indicates the apparatus that was used and figure 26 which gives some typical example of the variation in EEE during the grinding of an oxide copper ore. The variation in weighted average mesh size is plotted on the other axis for comparison. There seems to be no question that during most of the run the EEE data parallels the

mesh size curve indicating that the EEE is proportionate to the rate of grinding. This suggests that an EEE monitoring system might be used to follow the rate of grinding in an industrial plant. Studies of this process are continuing. We have adapted the EEE system to a one eighth scale continuous ball mill.

Another application of the EEE phenomena relates to the possible correlation between exoelectron emission and the induction of silicosis. In a series of studies we have demonstrated that freshly ground silica is a copious emitter of exoelectrons and that this emission level can be related to the ability of silica to lyse red blood cells. The lysis of red blood cells (RBC) is often used as an analog to the pre-silicotic effects in the human lung and we have used this as a screening technique to evaluate silica and silica materials under a variety of conditions. Here again the results have been given in some detail elsewhere (reference 7 ) and we will only mention some primary results.

A correlation exists between the ability of silica to lyse RBC and the EEE level of the silica after grinding. In an industrial situation the silica may become either more or less effective in terms of the RBC test depending upon what metals are in the environment. Typically iron raises the rate of lysis and aluminum reduces it. This effect has been noted industrially and the addition of aluminum to mine environments is common practice in Canada and South Africa. The effect of silica particles on RBC is not yet fully understood but is thought to involve the formation and destruction of a protein layer by macrophage action in the lung.

#### Catalysis Studies.

The investigation of catalysis by means of EEE has been reported

several times in the literature but the technique is not yet used by many investigators. A review of the literature in this area has been given in reference 8 which also discusses our own work in some detail. Only a few highlights, to demonstrate what sort of experiments can be done, will be reported here. Our experiments were done in a vacuum system monitored by a quadrupole mass spectrometer. The catalysts were in the form of filaments of various metals. The EEE during catalysis was monitored by the usual collector and picoammeter arrangement, no ultra-violet source was used. The gases involved were H<sub>2</sub>, CO, NH<sub>3</sub> and NO; the catalysts were commercial platinum or palladium while monel was used for the NO plus CO reaction. Typical reactions for H<sub>2</sub>, CO or NH<sub>3</sub> involved oxidation under either "rich" or "lean" conditions.

Typically, the gas mixture was stabilized in the system and the catalyst was heated to begin the reaction. Once the reaction had started the gases were bled in at whatever rate was needed to keep the system in a steady state. The EEE was measured as the reaction proceeded and we were able to demonstrate that in every case the rate of reaction could be monitored in terms of the observed rate of EEE. In the case of the monel catalyst, where the heating rate has an important effect on the steady state rate of reaction, we were able to follow the rate-of-heating effects during start-up and predict the steady rate of reaction. Typical results with a monel catalyst for the CO plus NO reaction are shown in figure 27 where we have plotted the rate of catalysis (K) and the rate of EEE versus time. The heating rate work is shown in figure 28 where we have plotted (K), the EEE current, I<sub>e</sub> and the filament temperature versus time. It is clear in both of these figures that we can follow the rate of reaction and in the case of figure 28 predict the steady state rate of reaction from the EEE level during the heat-up phrase.

General Conclusions.

While many questions about EEE still remain to be answered, we can expect that the technique will find wide application in a number of areas.

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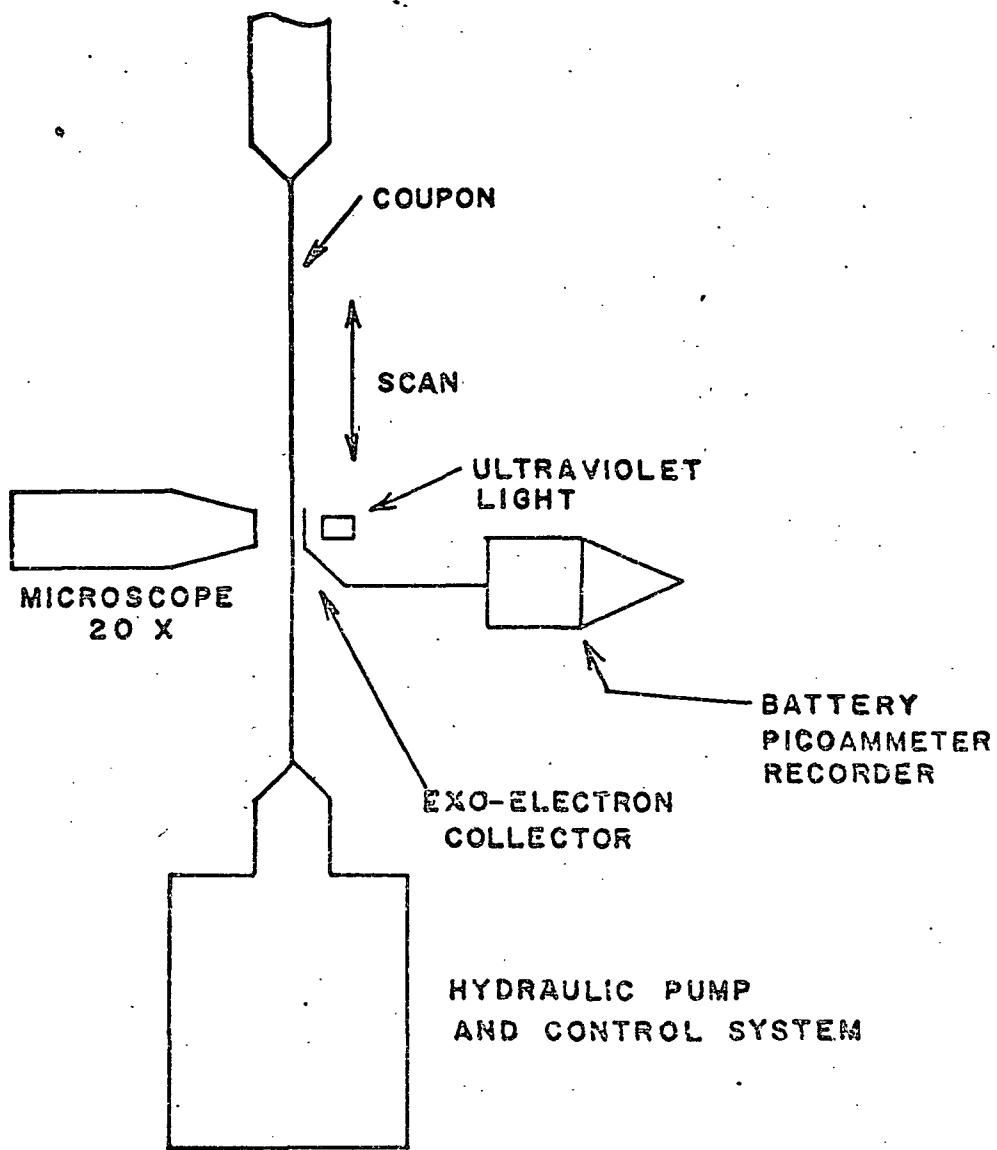
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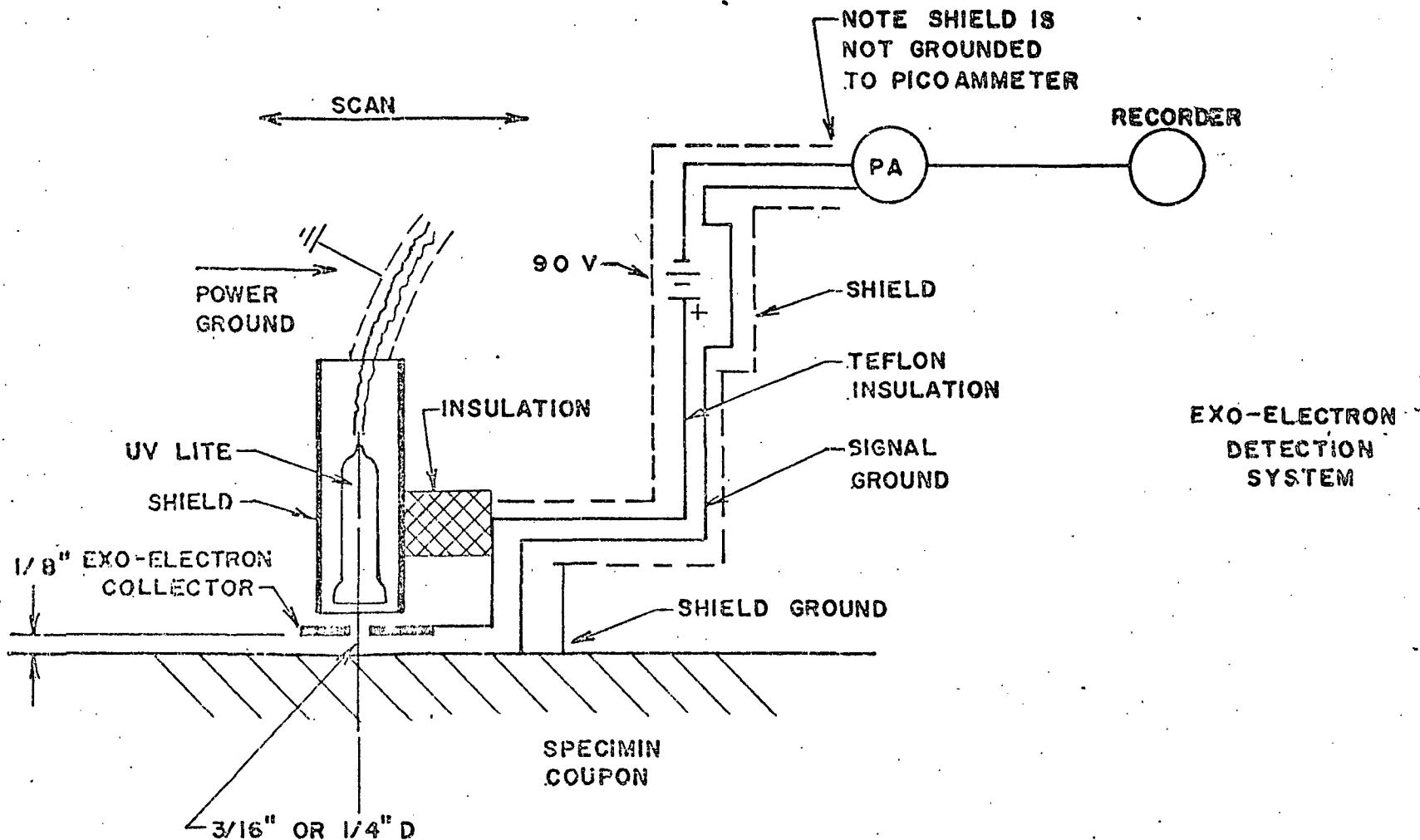
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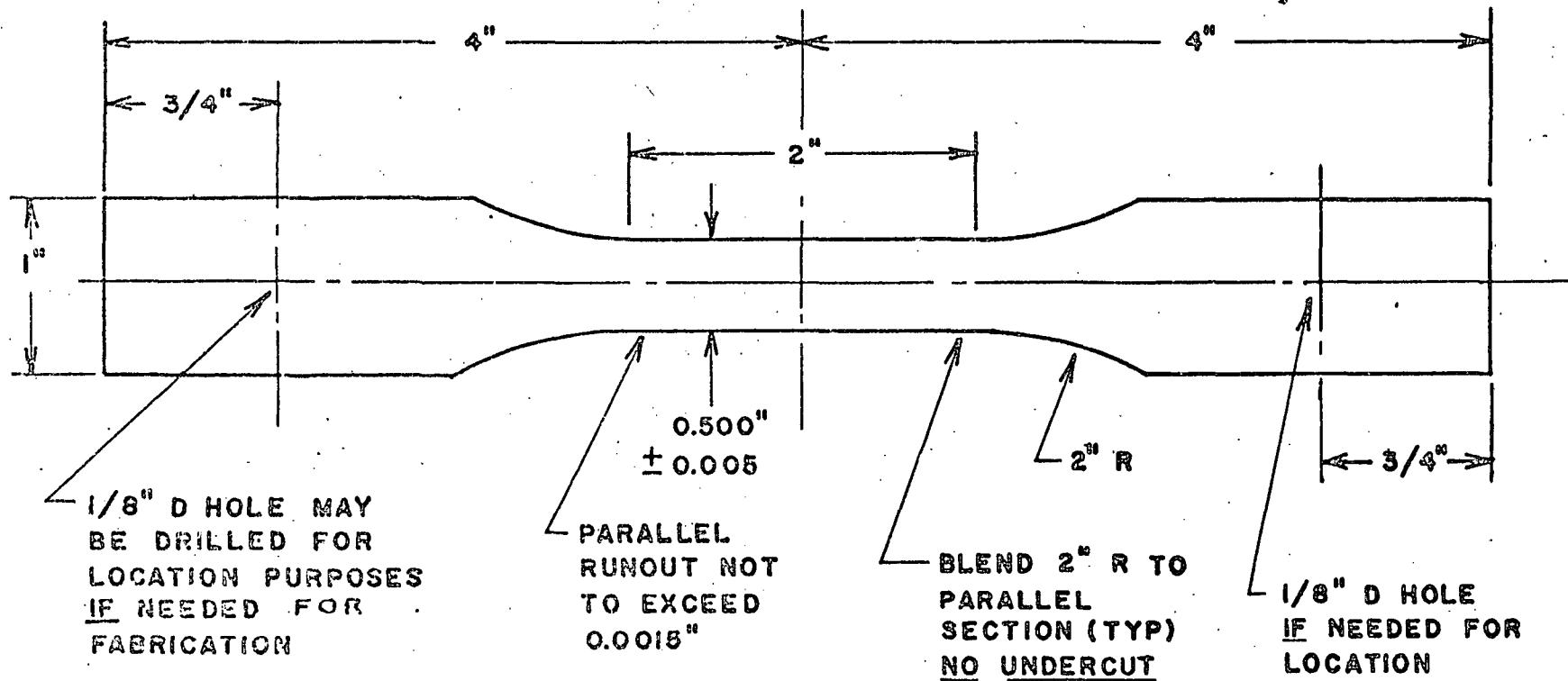
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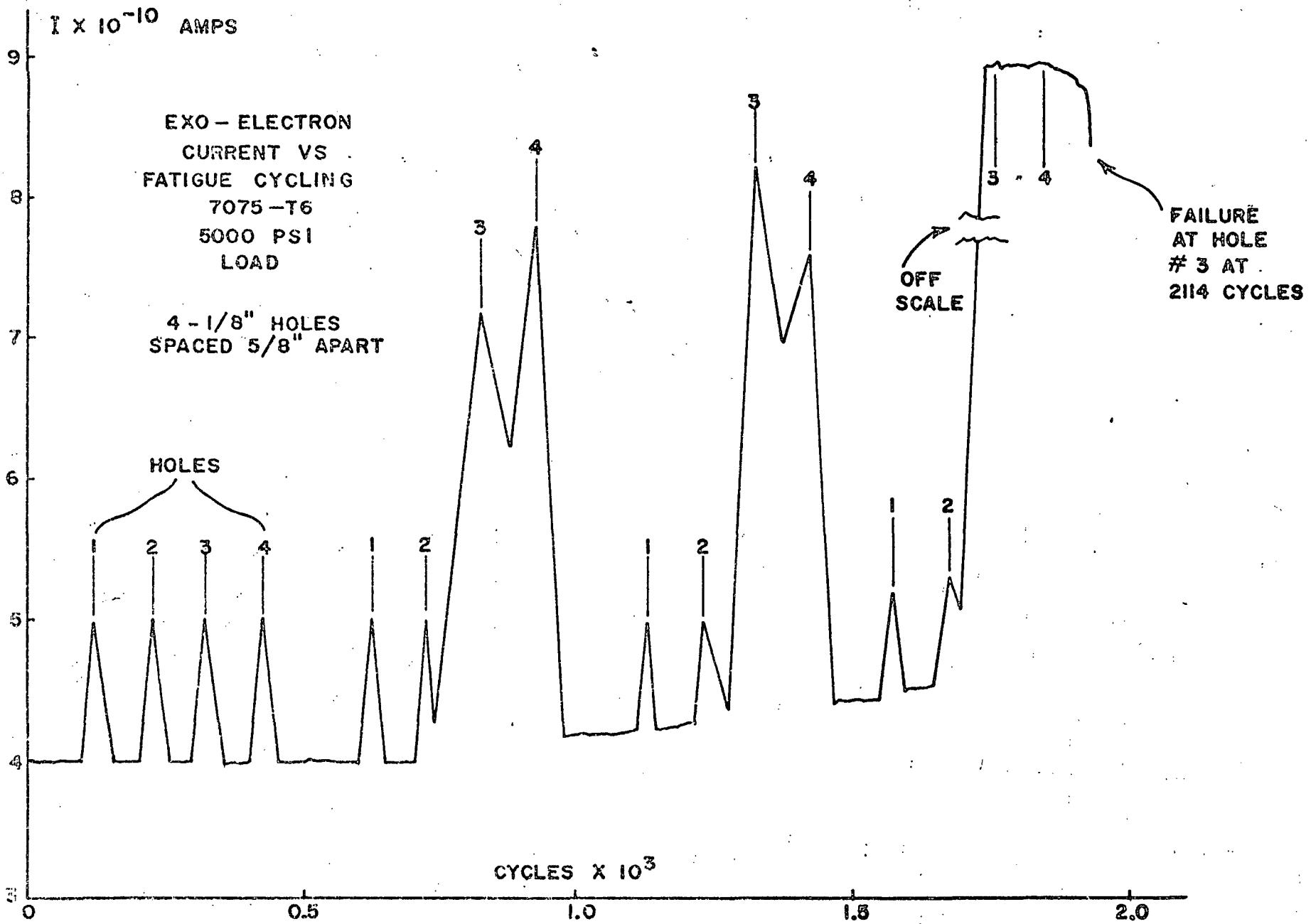


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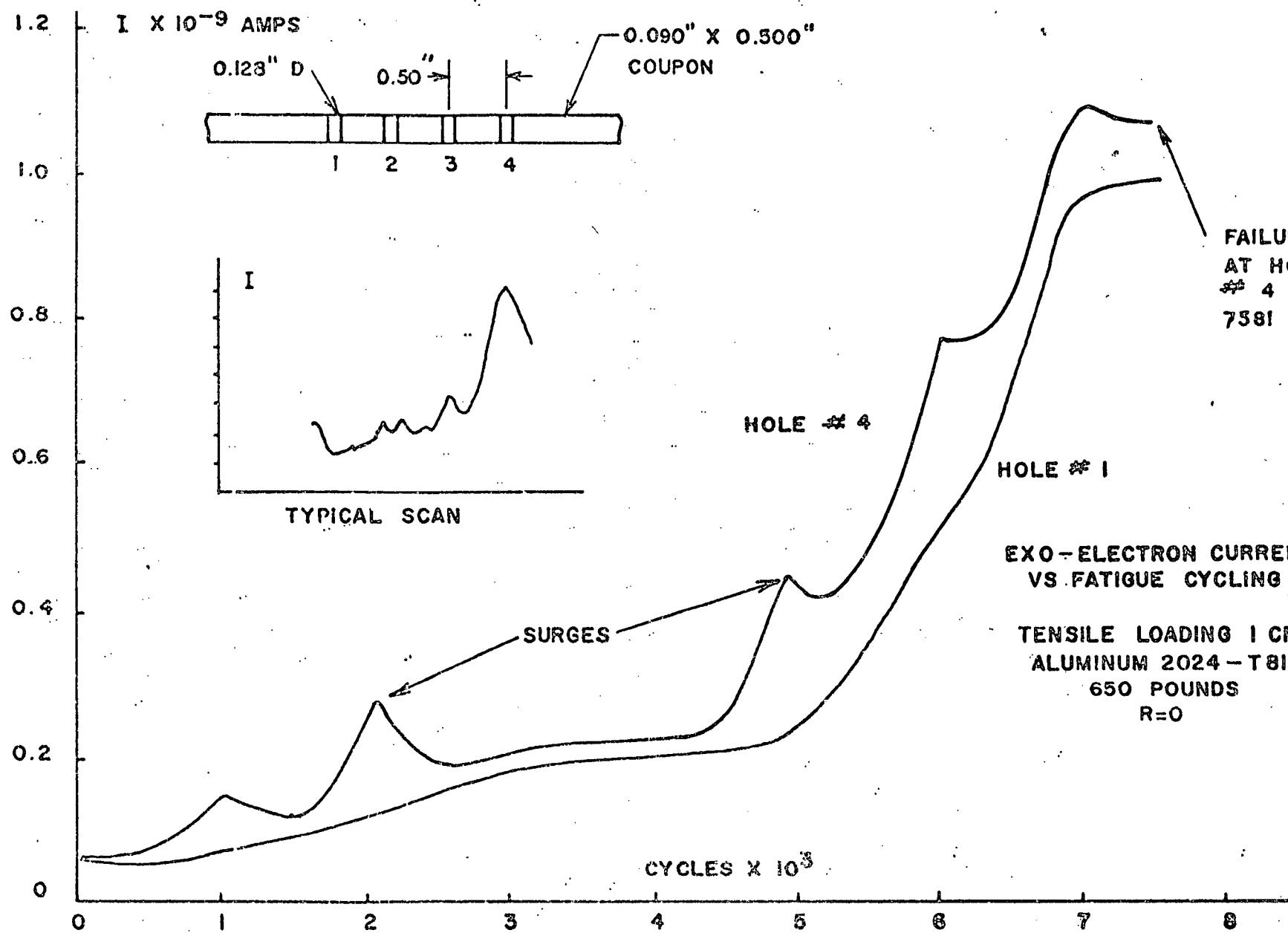


### TEST COUPON CONFIGURATION

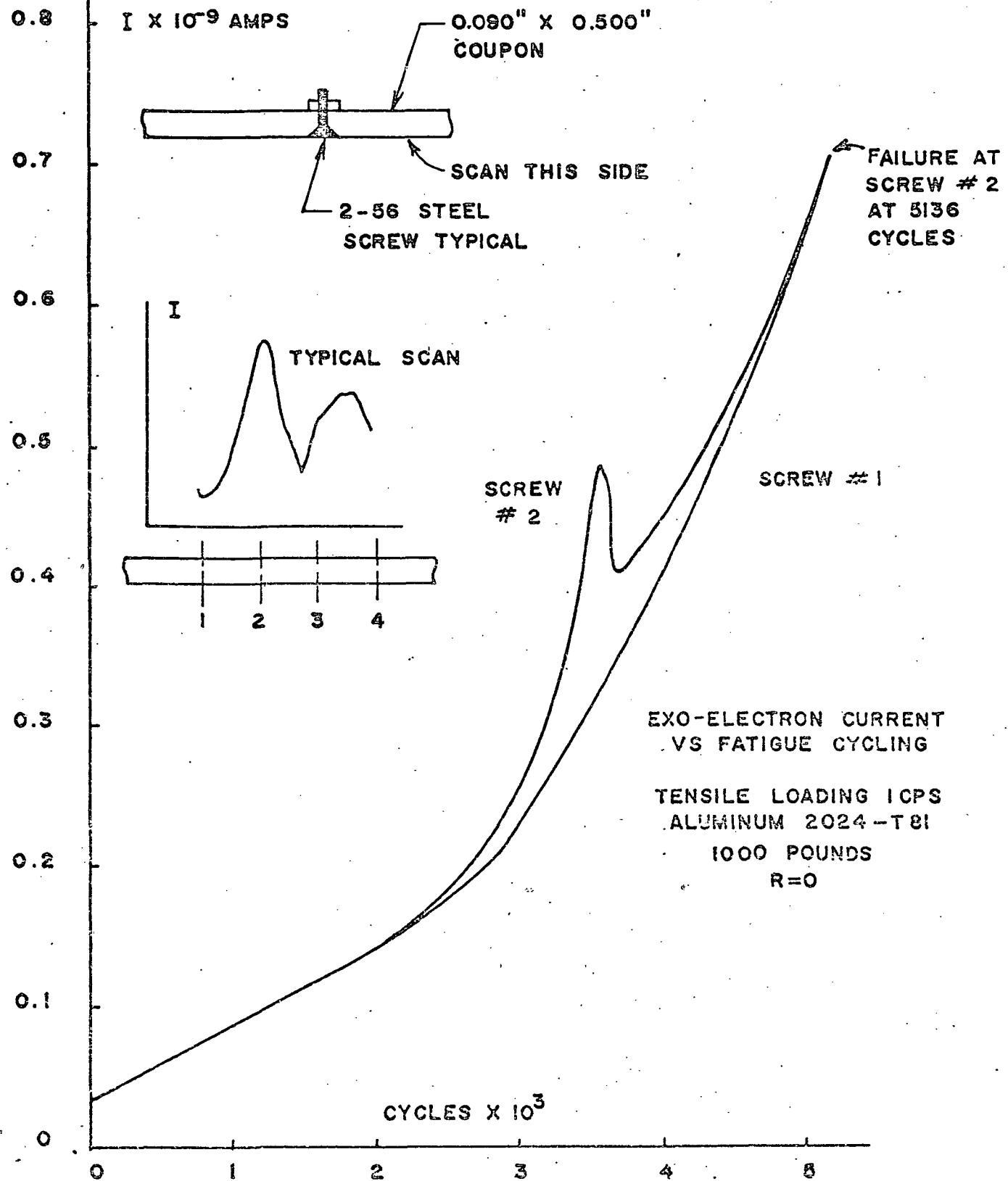


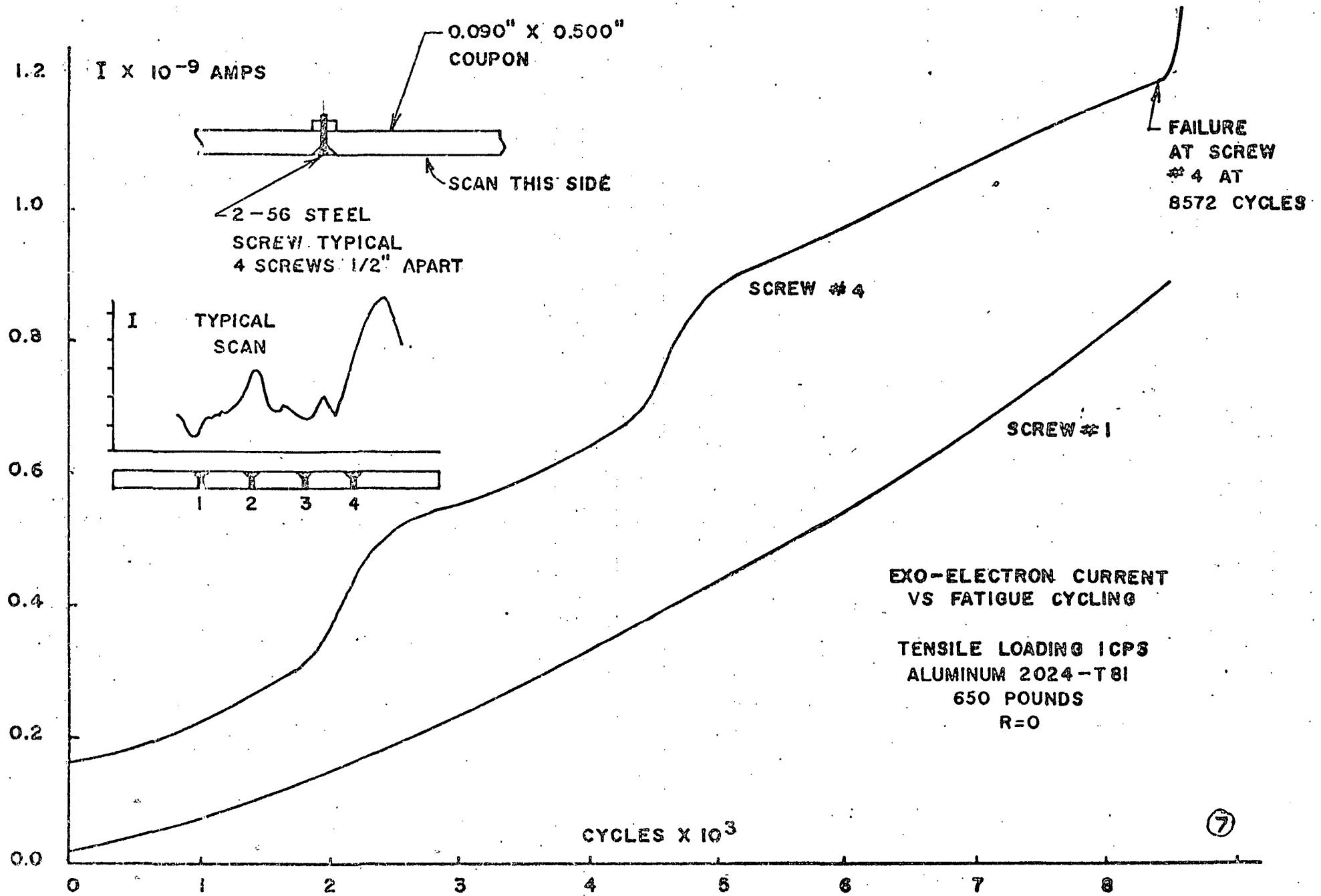


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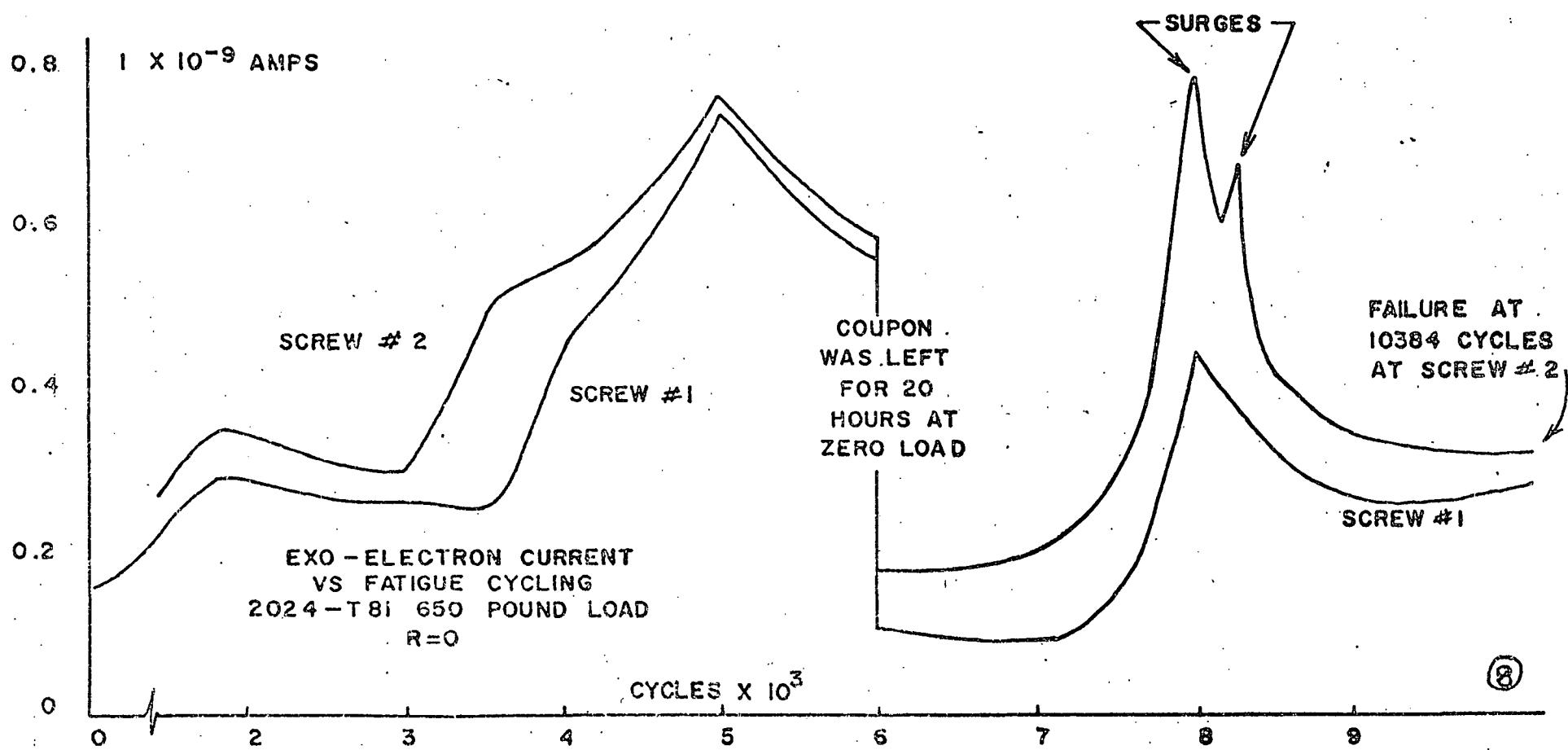
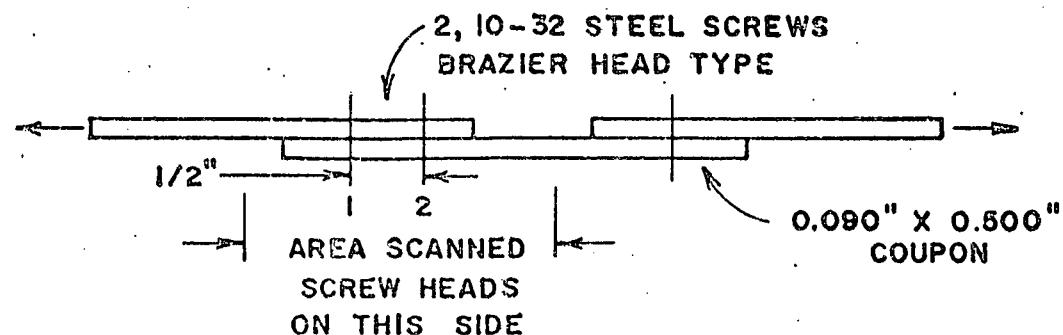


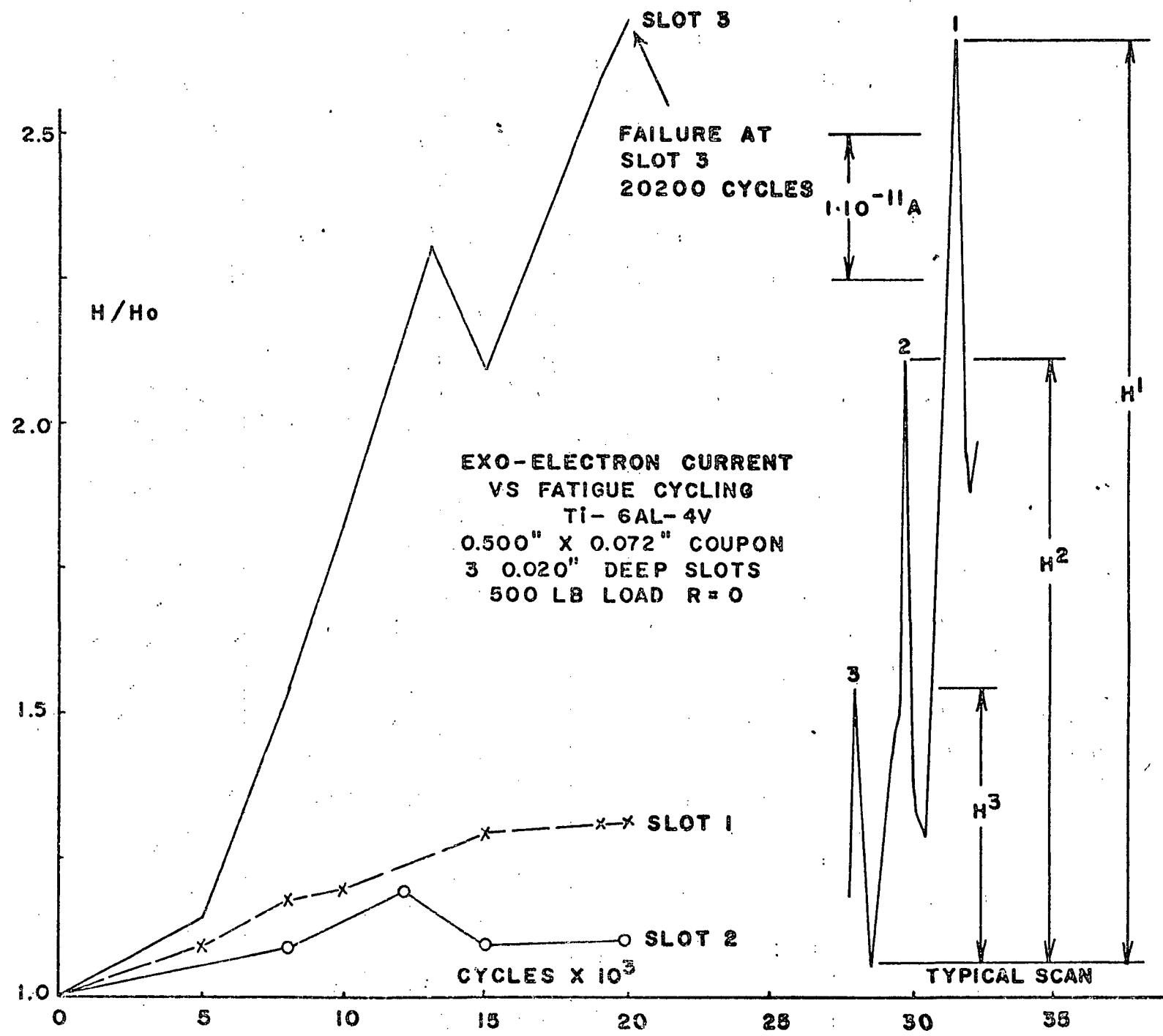
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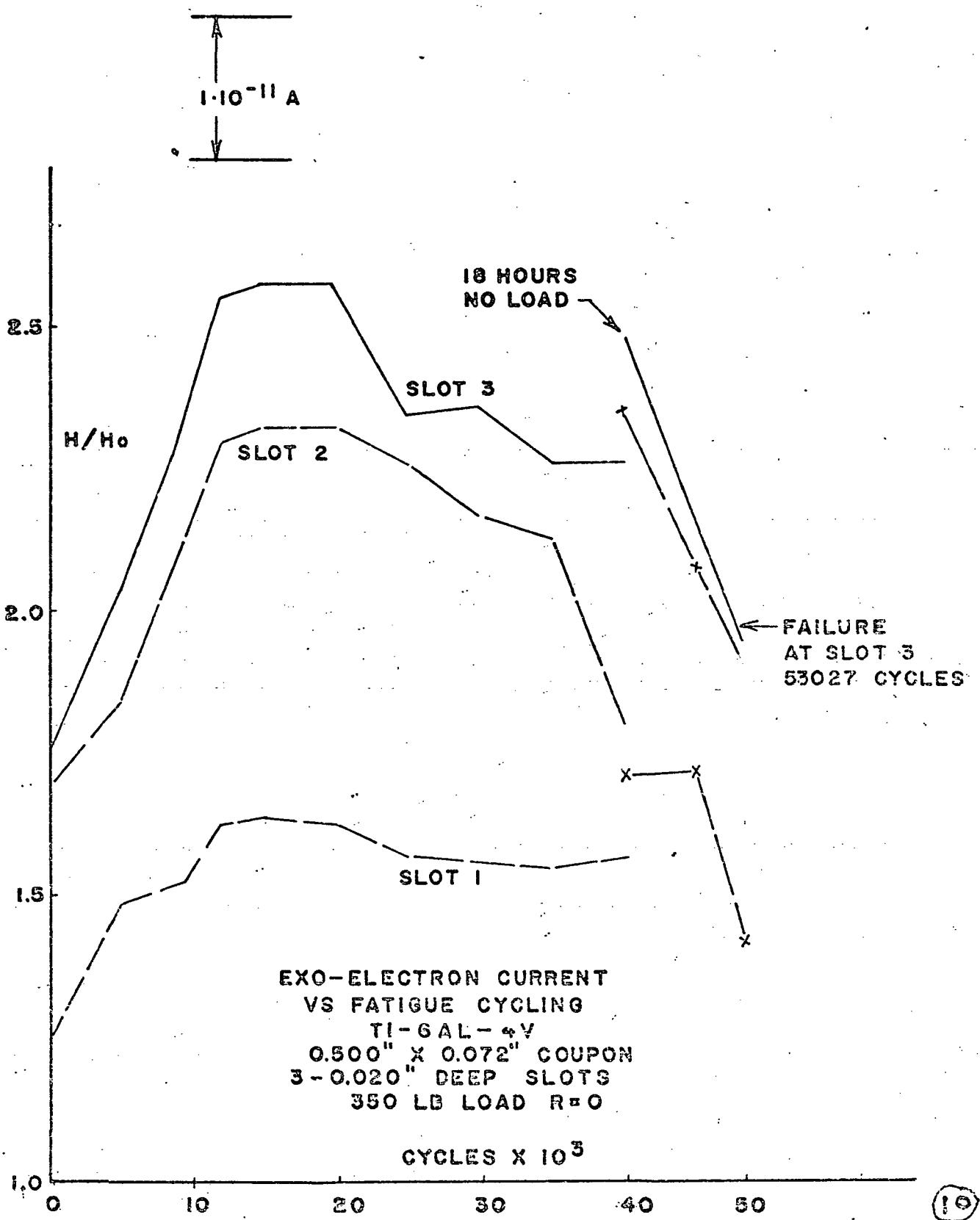


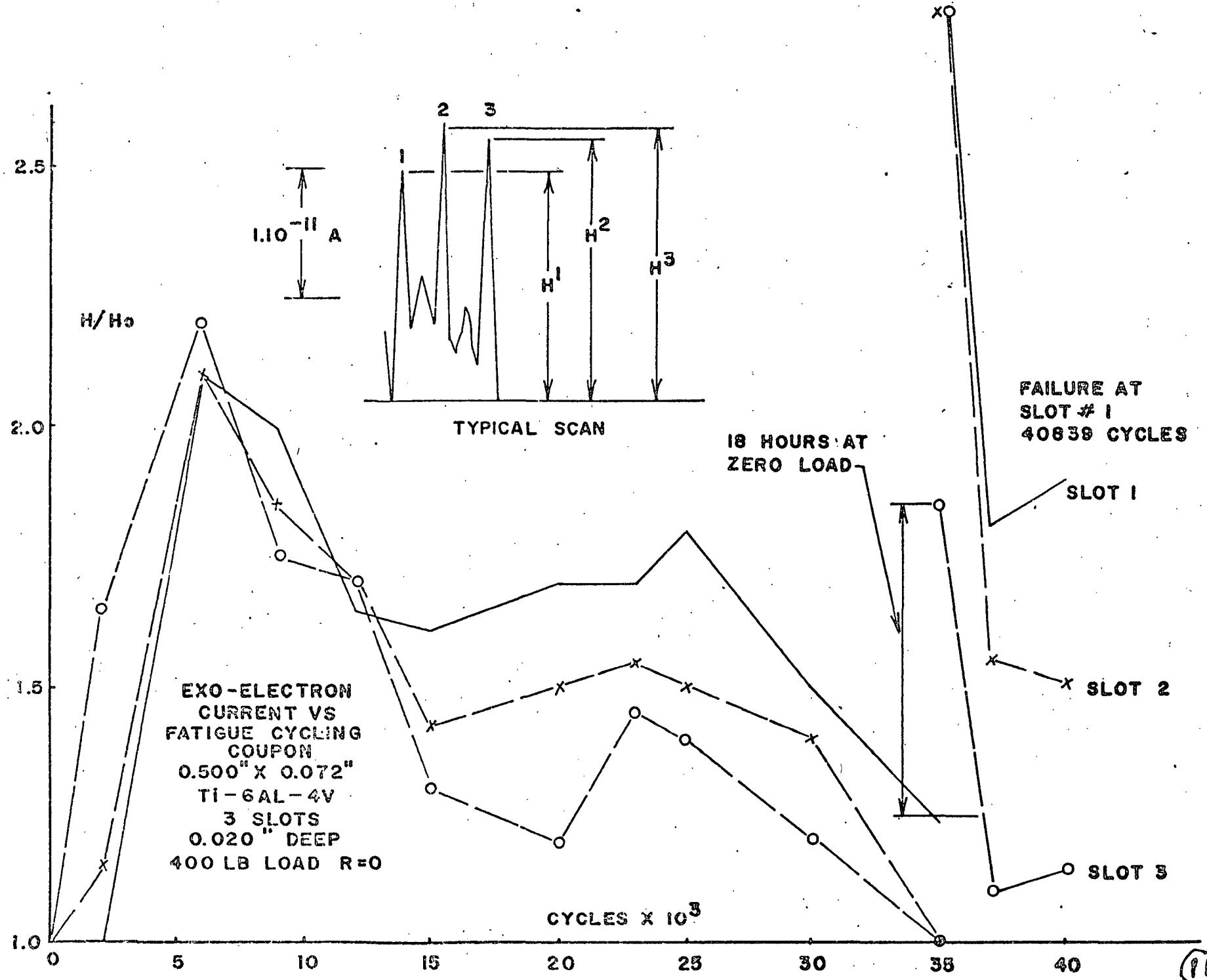


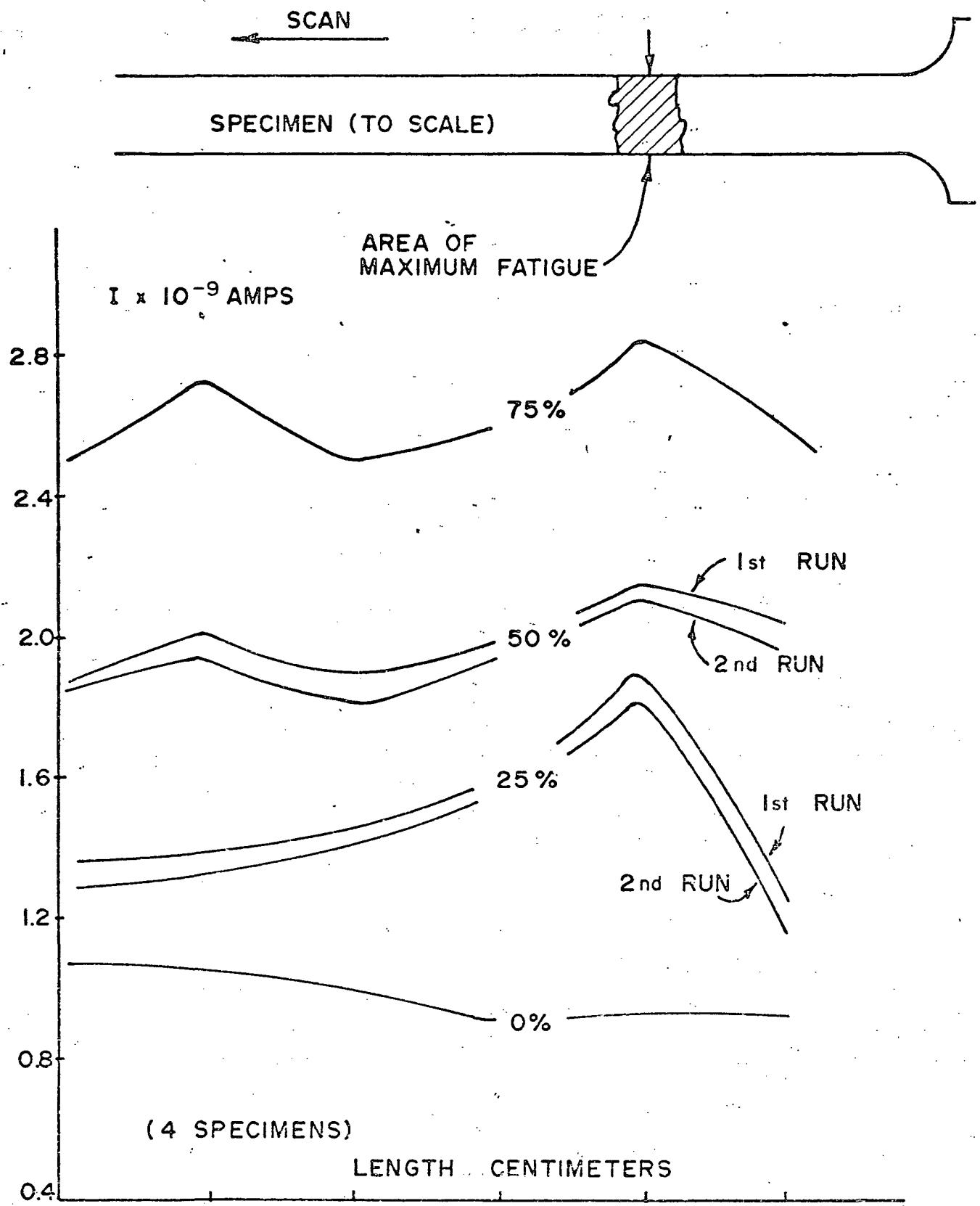
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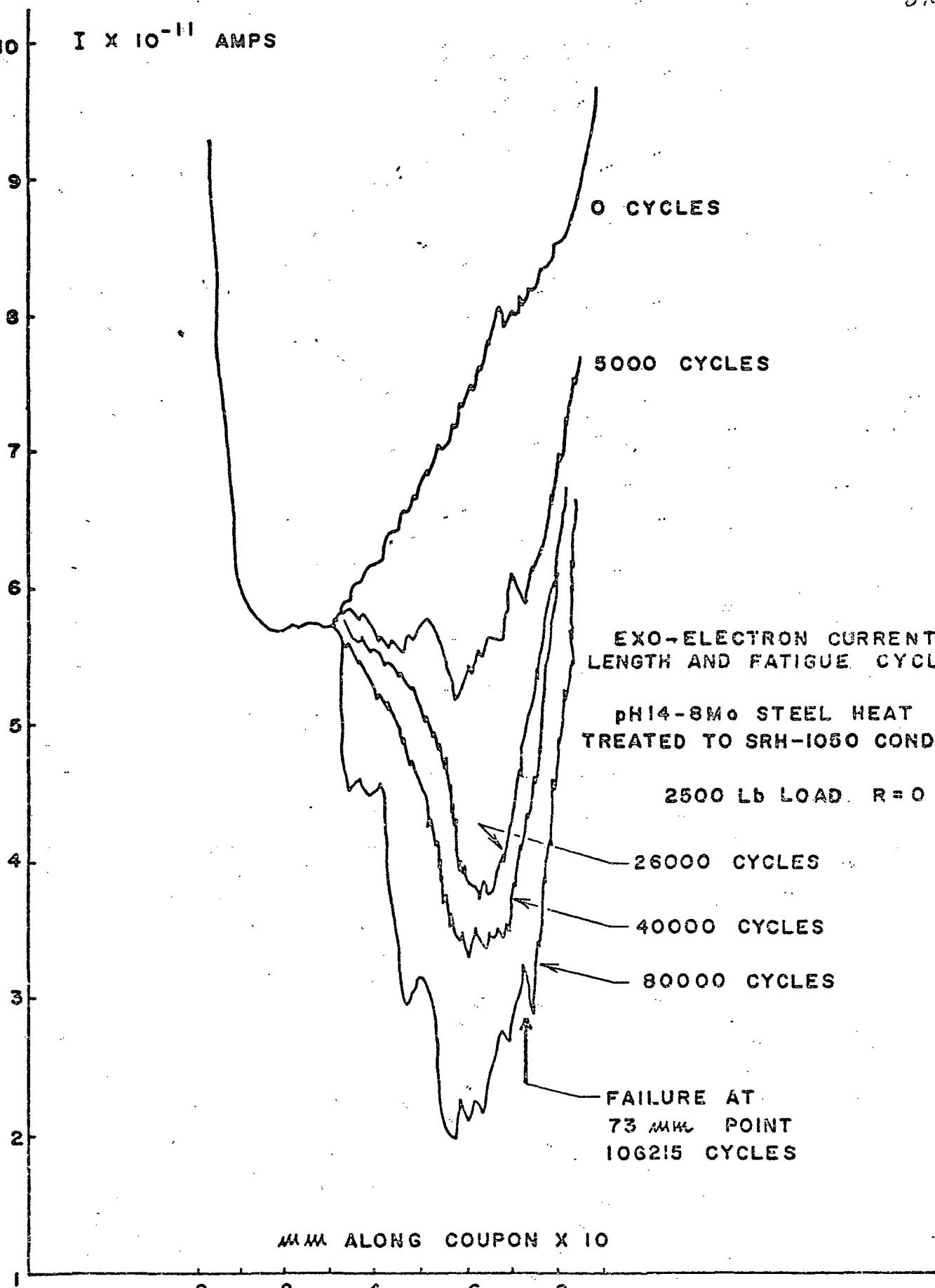


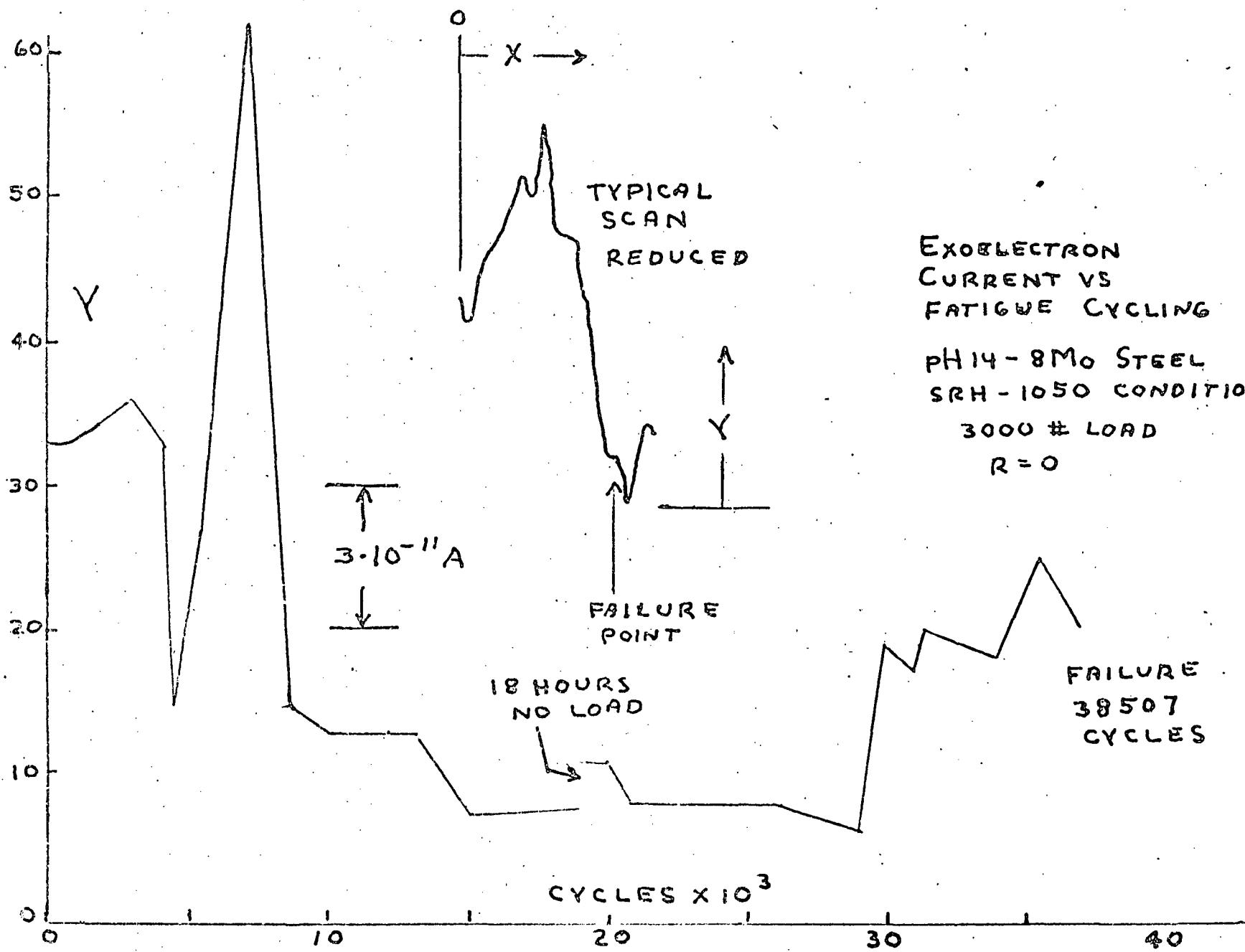


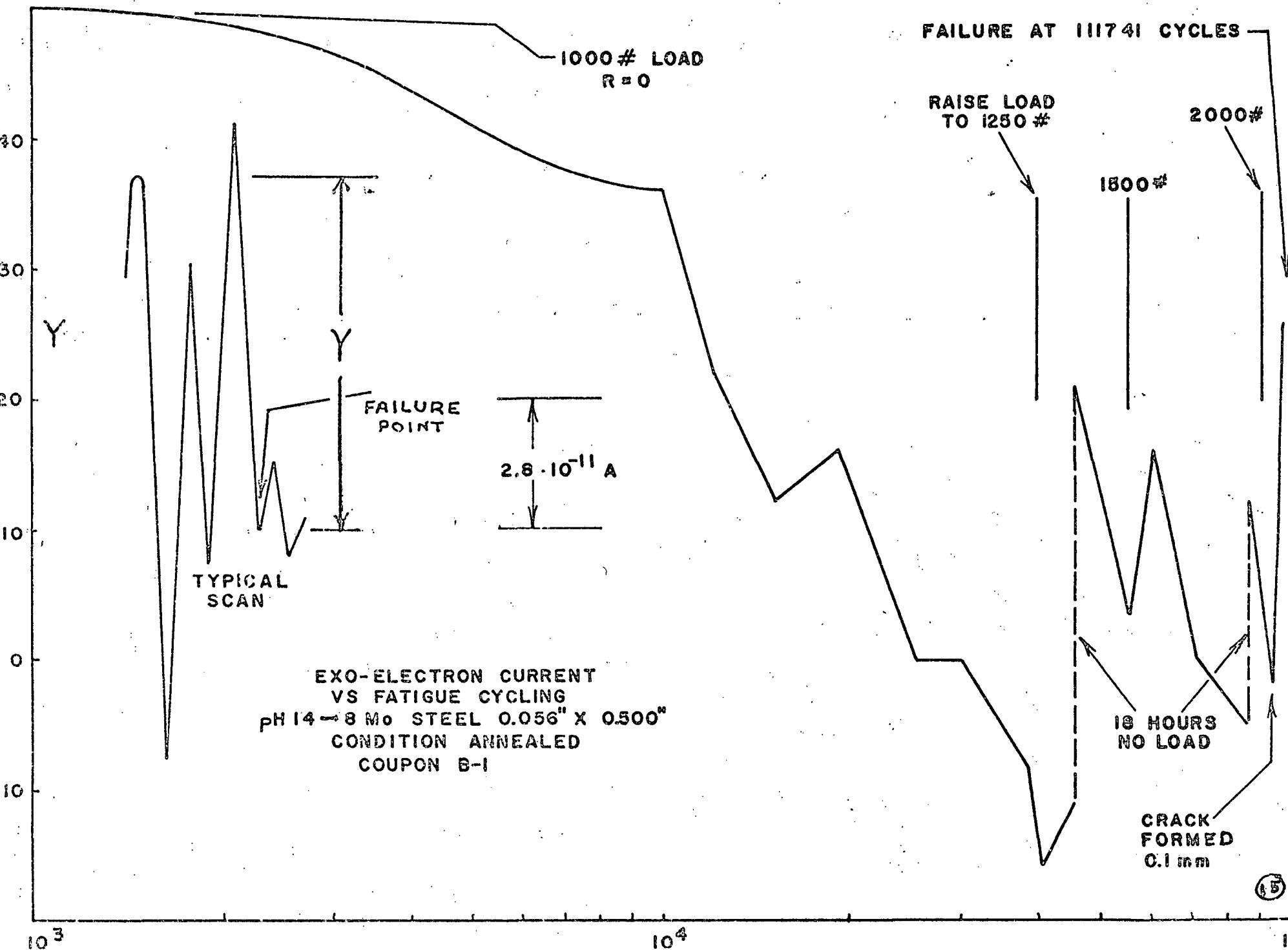


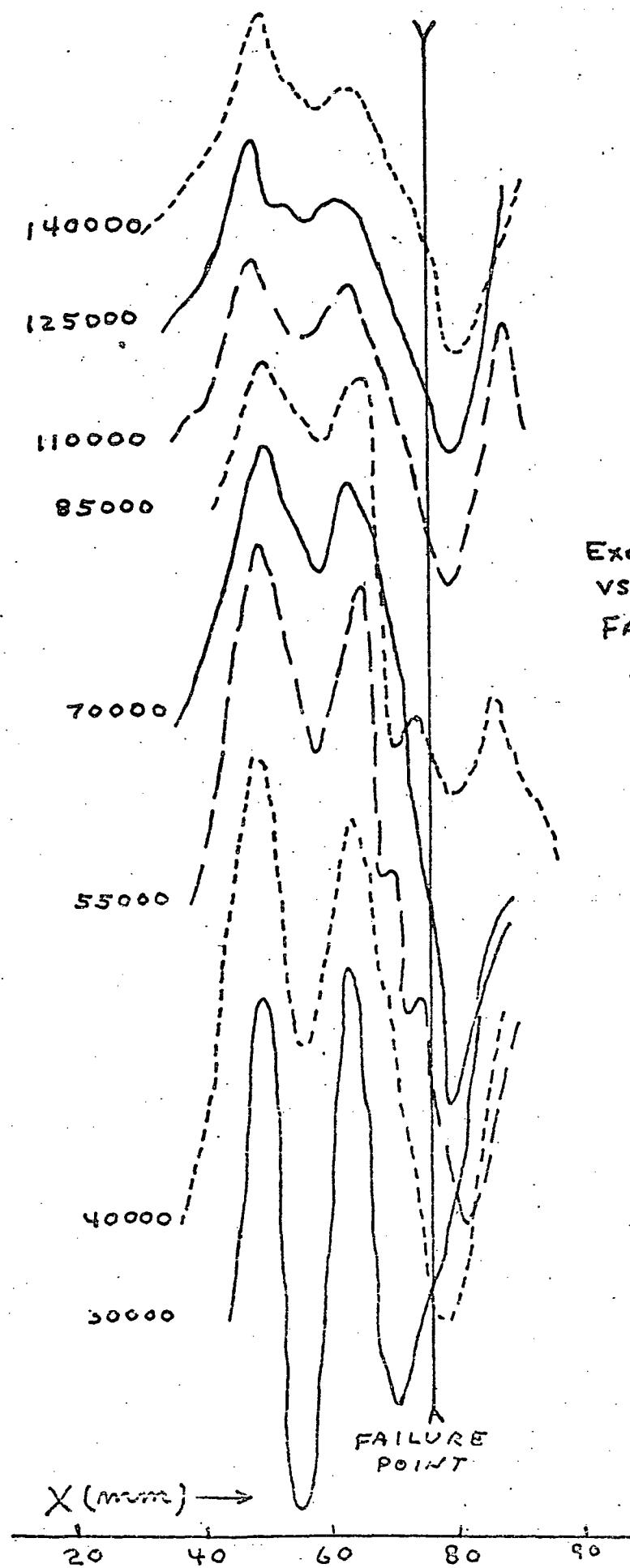
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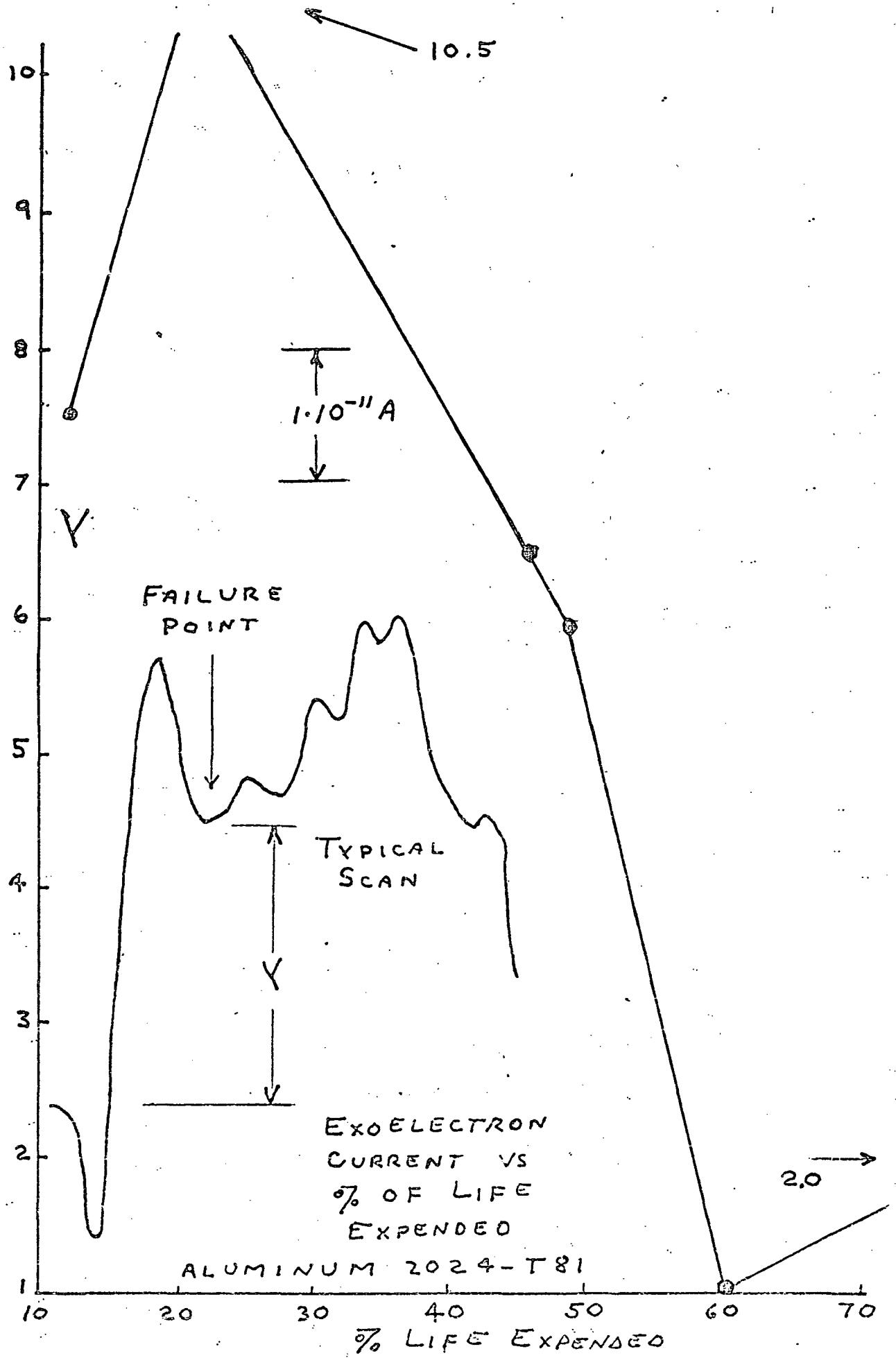
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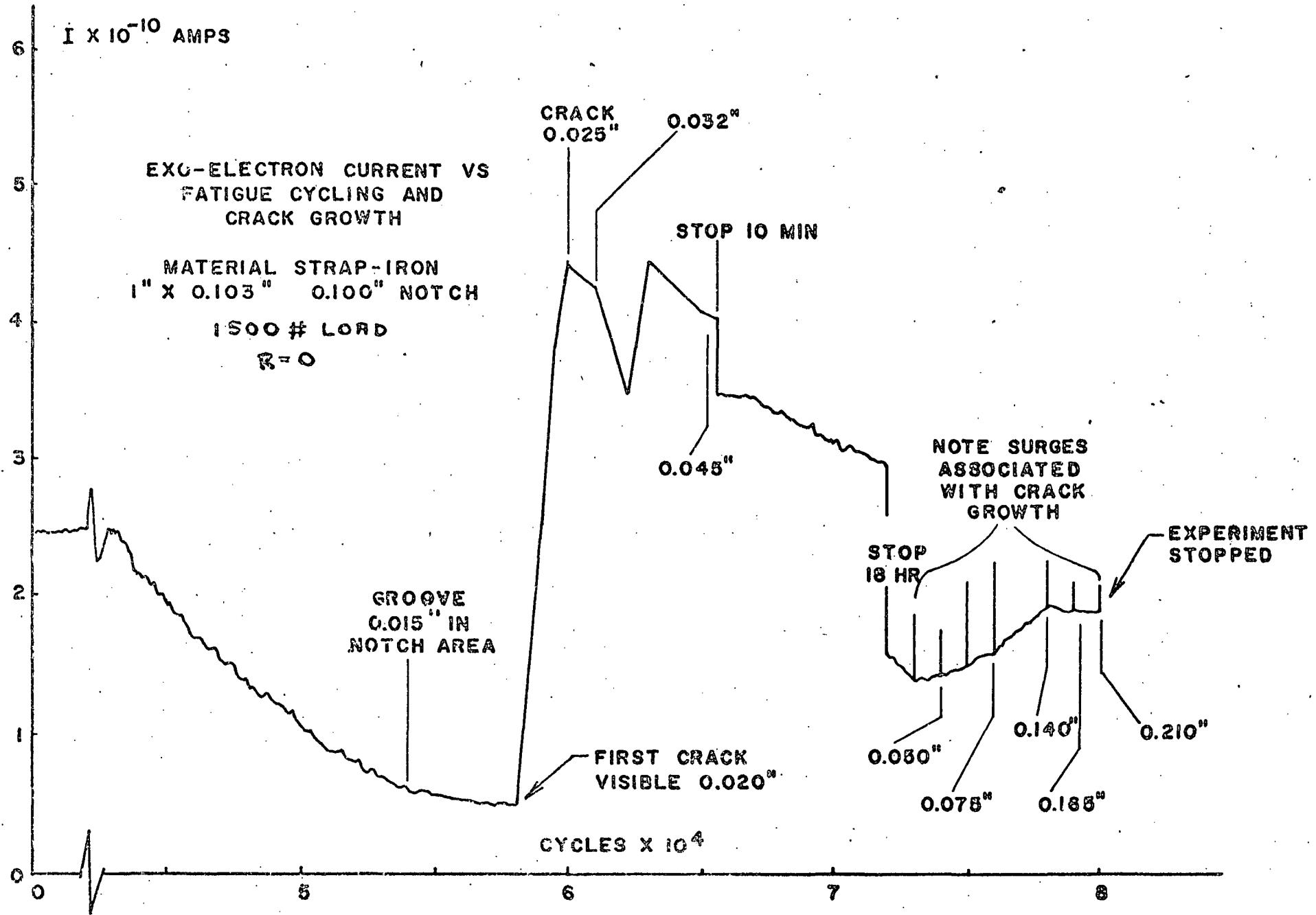


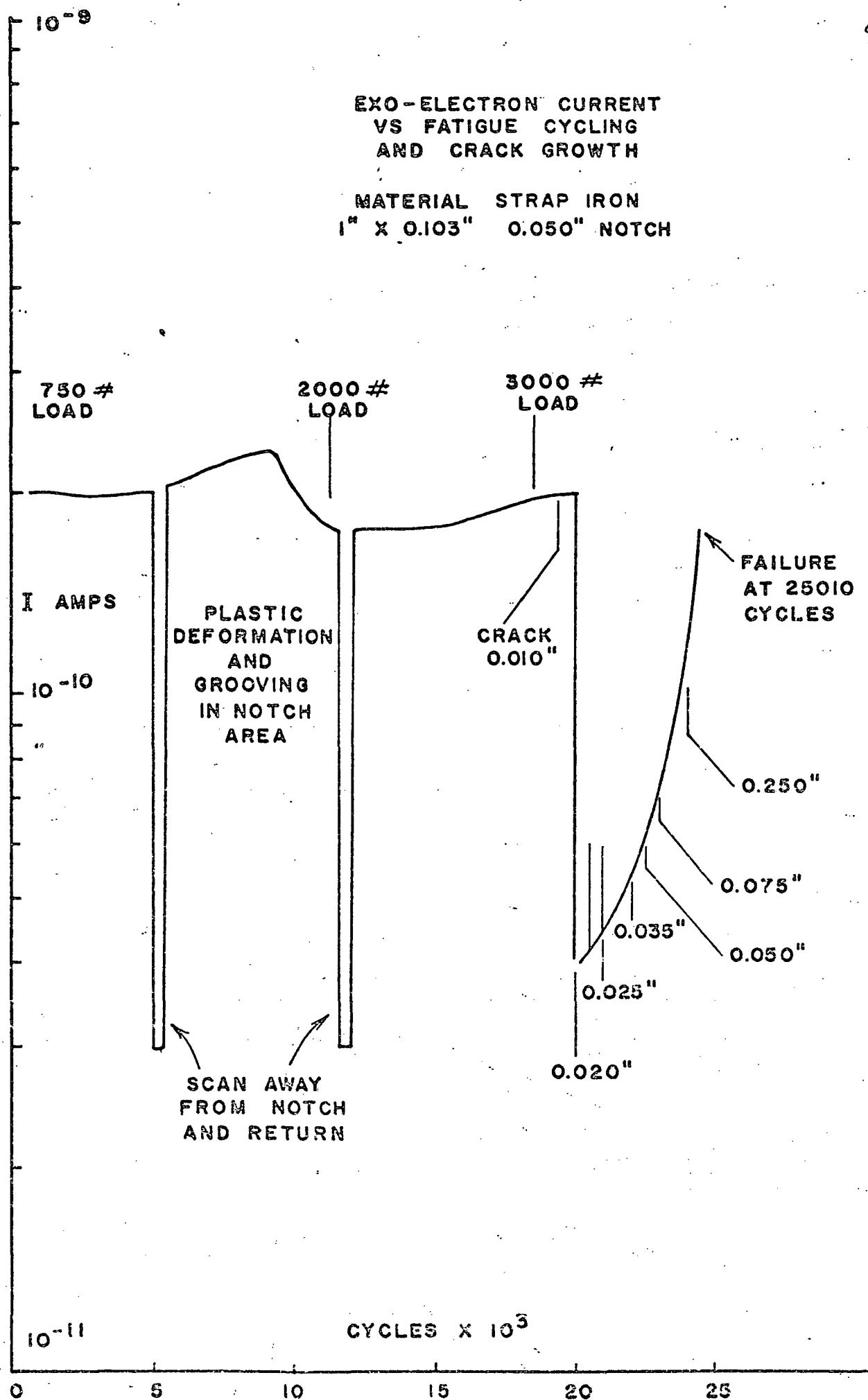


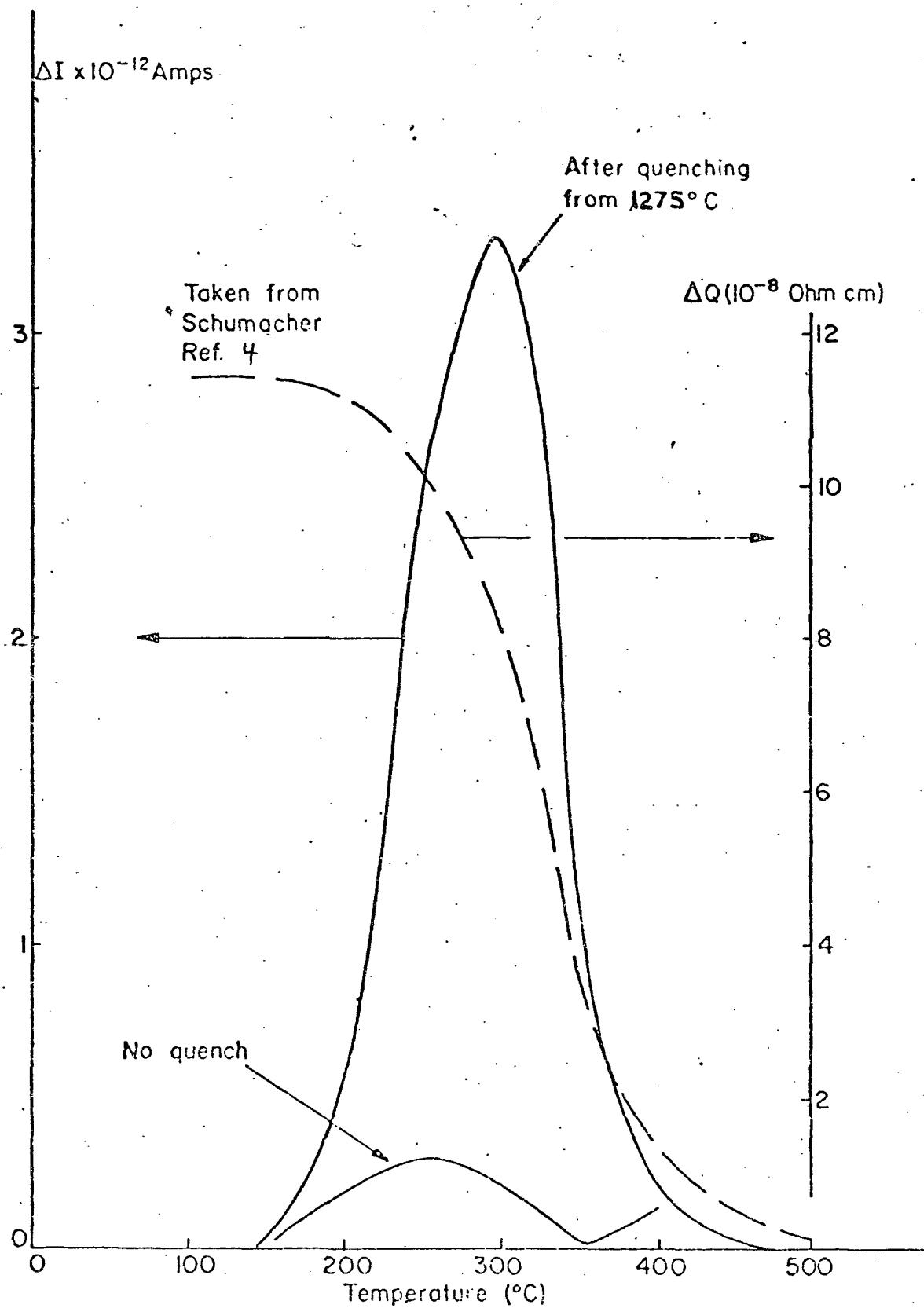




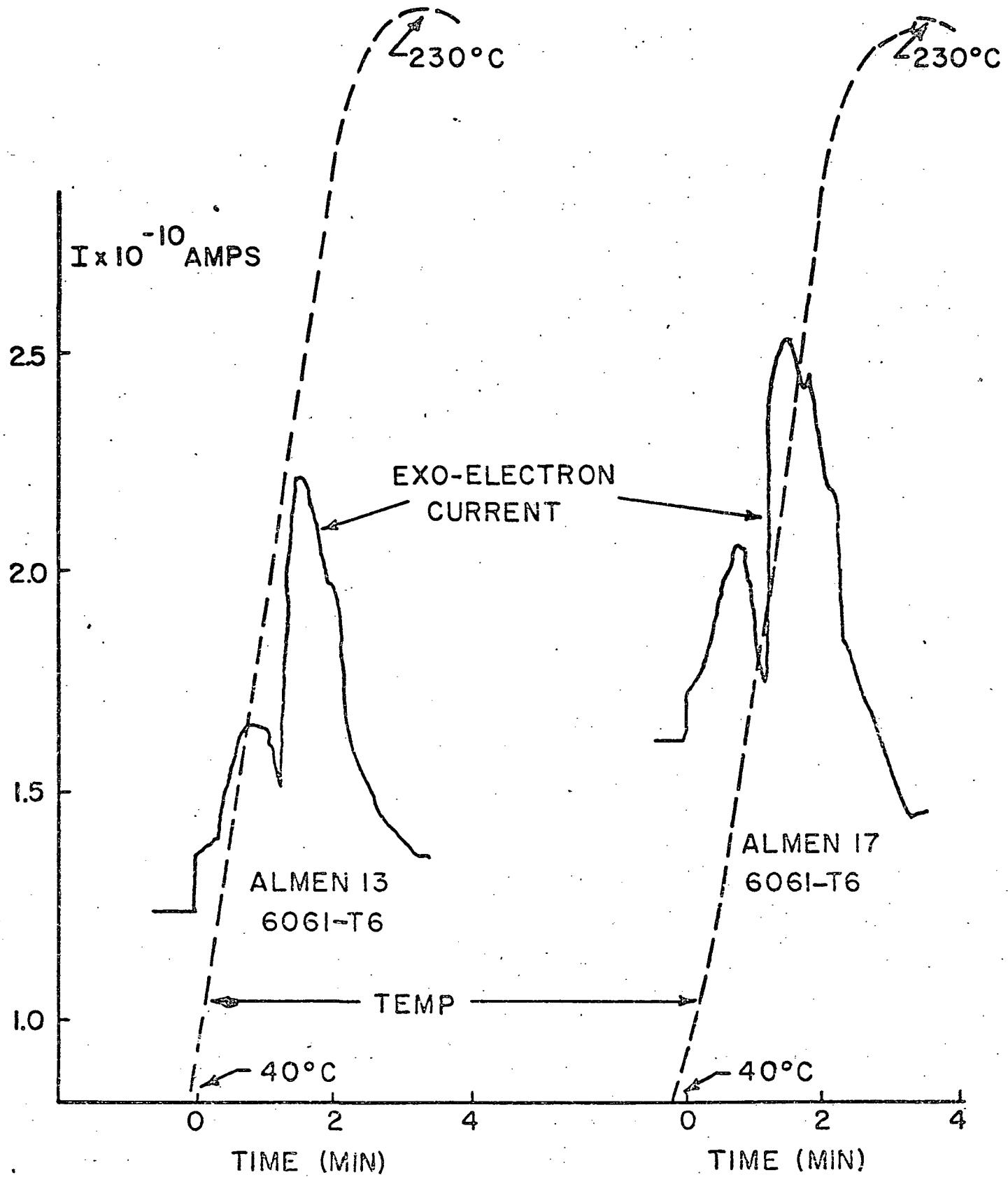




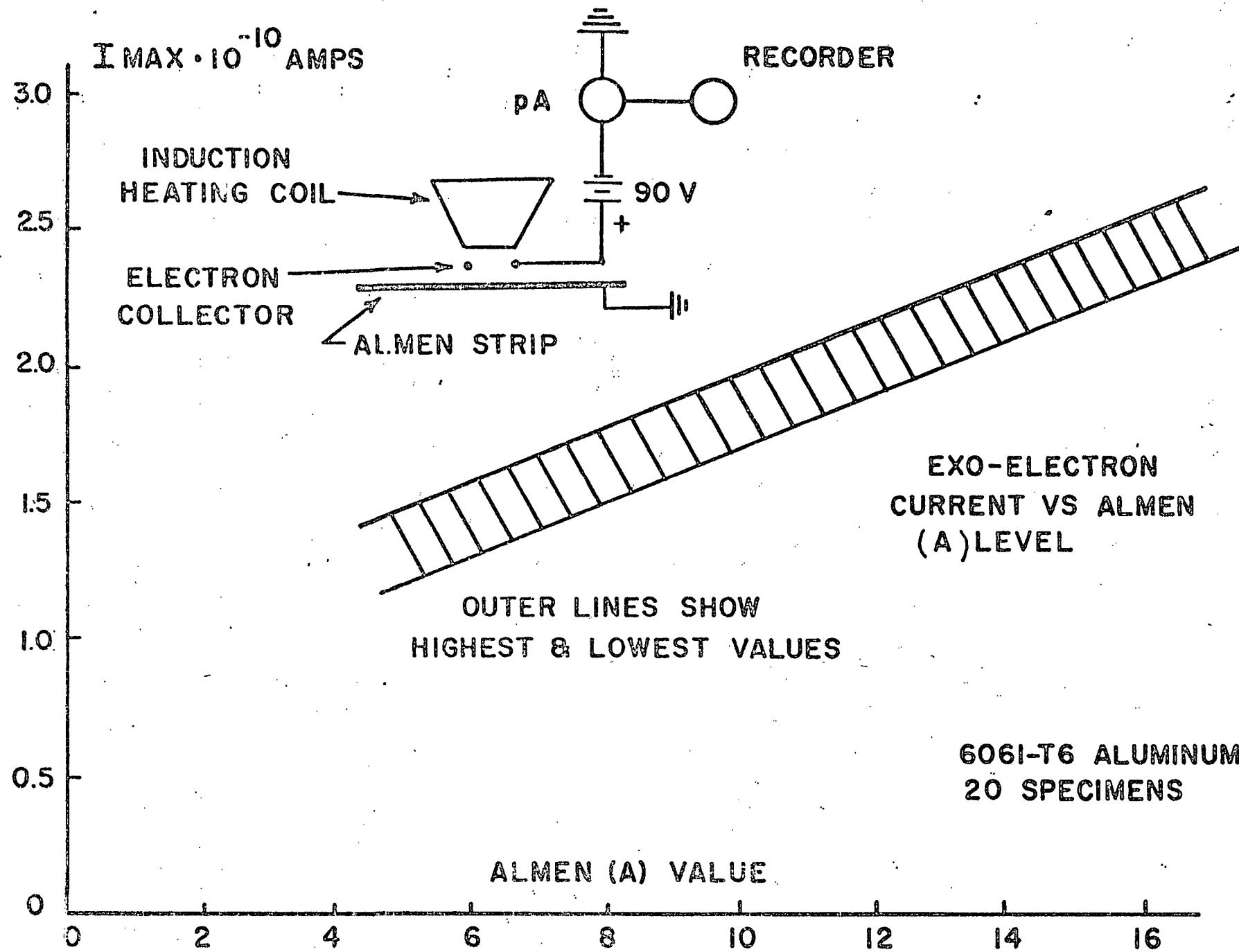


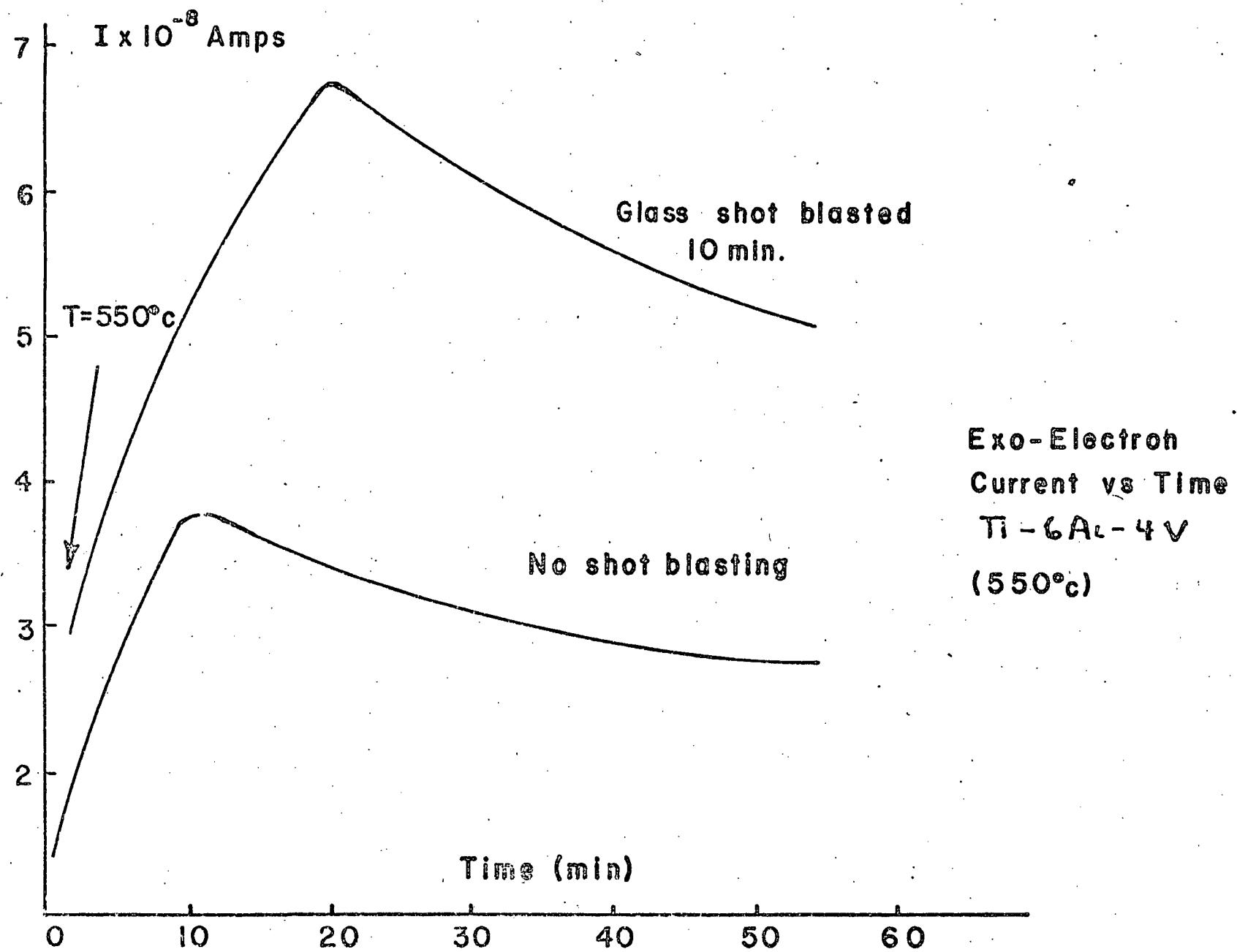


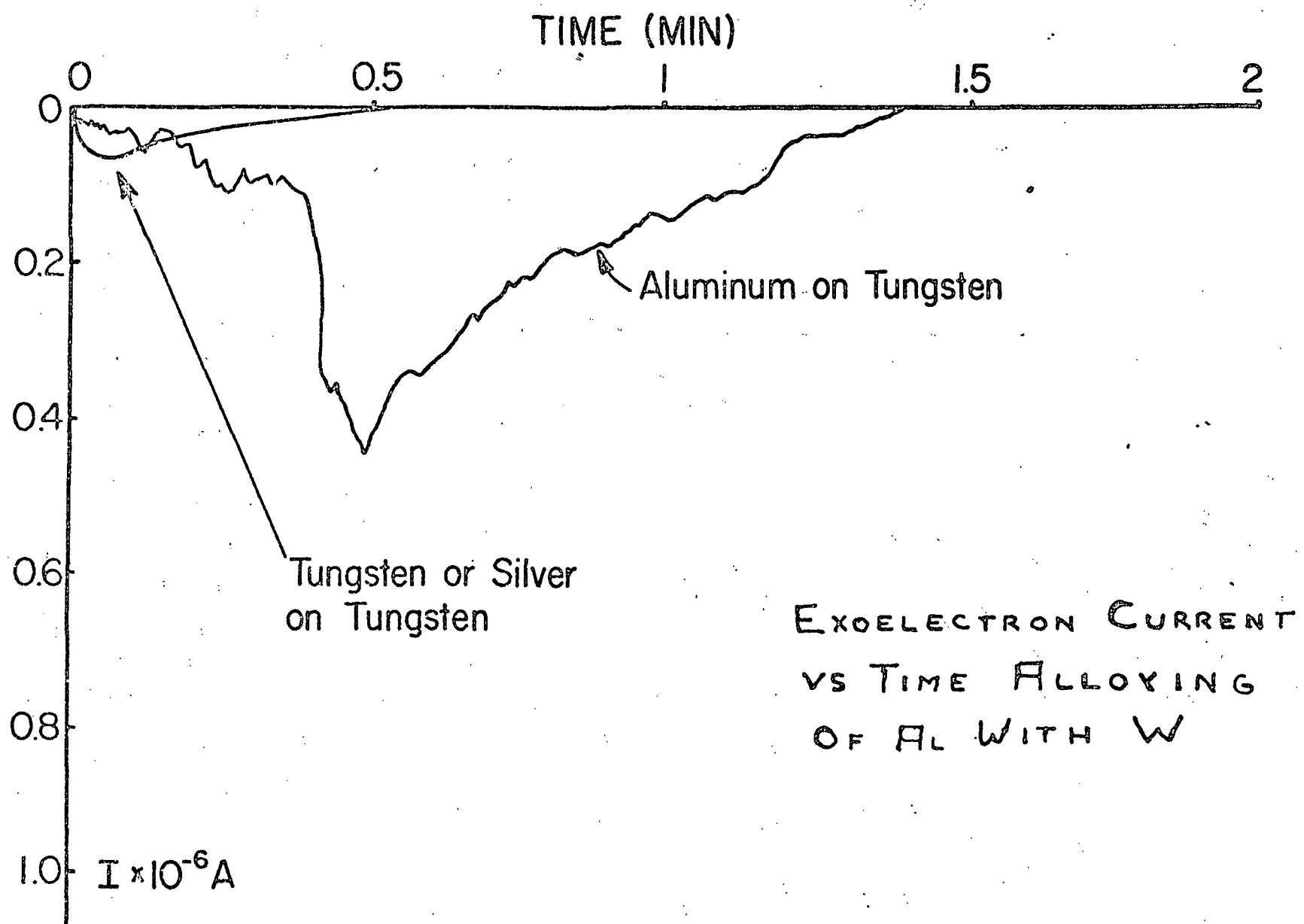
$\Delta I$  VS TEMPERATURE  
 (ISOCHRONAL ANNEALING)

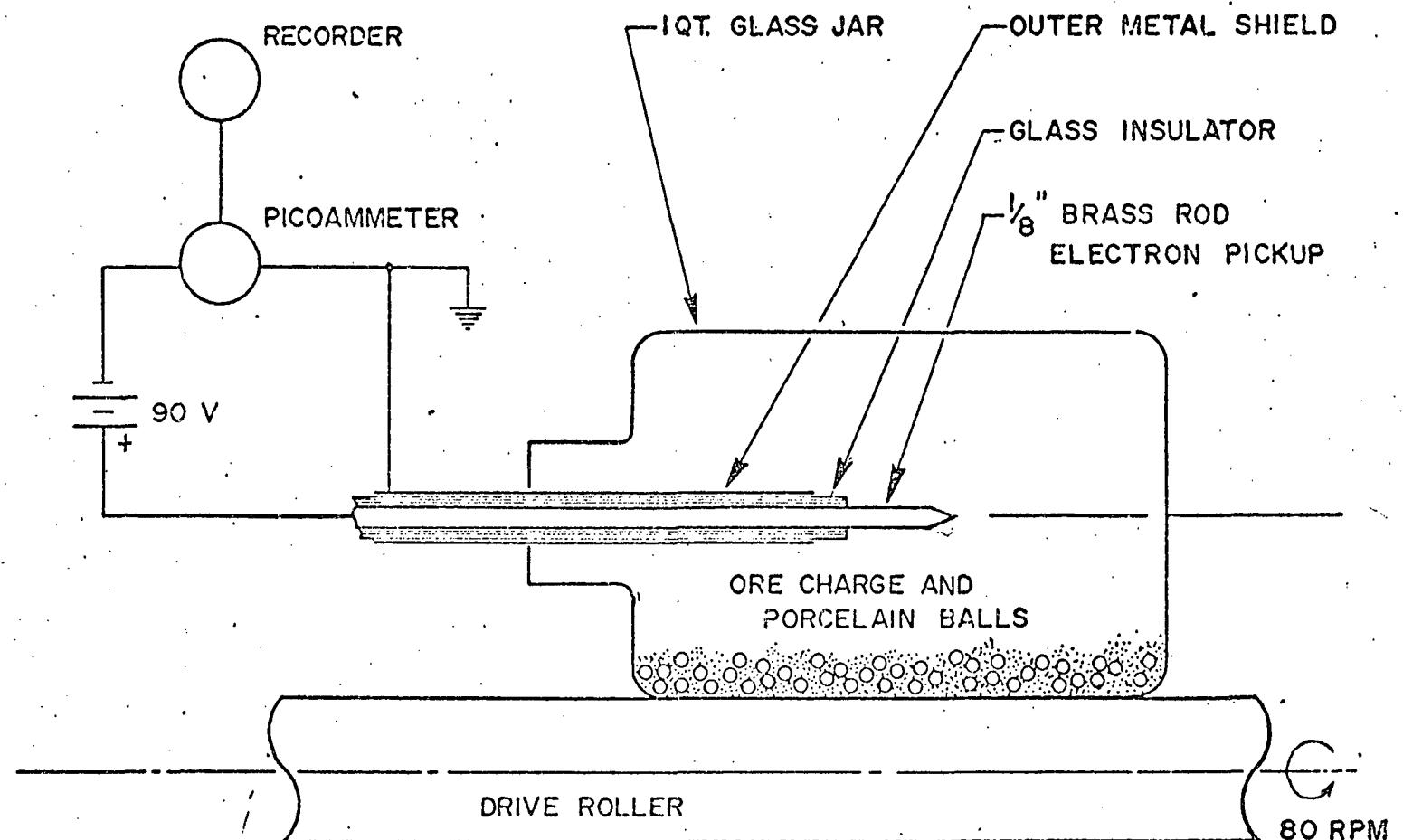


EXO-ELECTRON CURRENT VS  
TIME & ALMEN (A) LEVEL

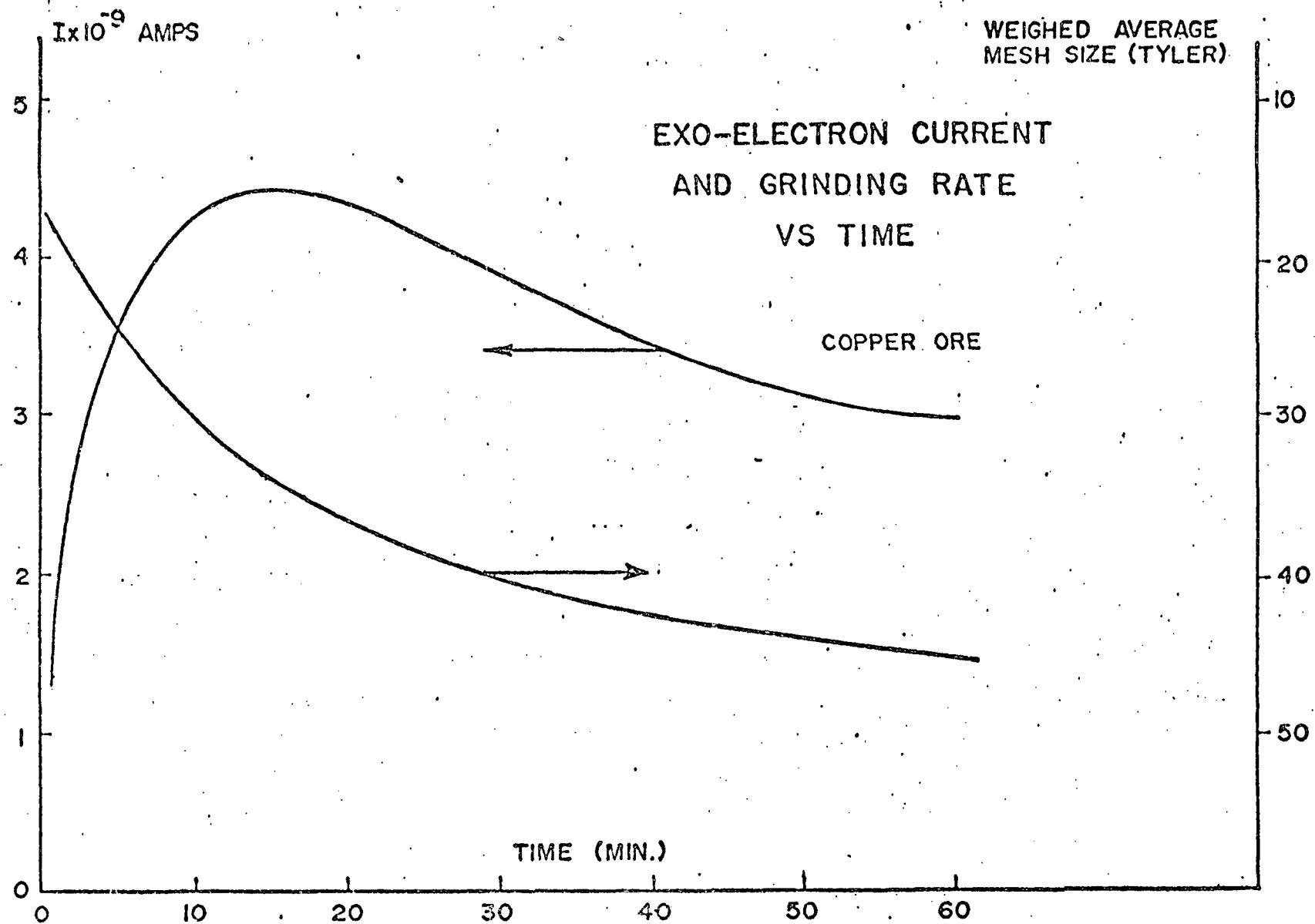




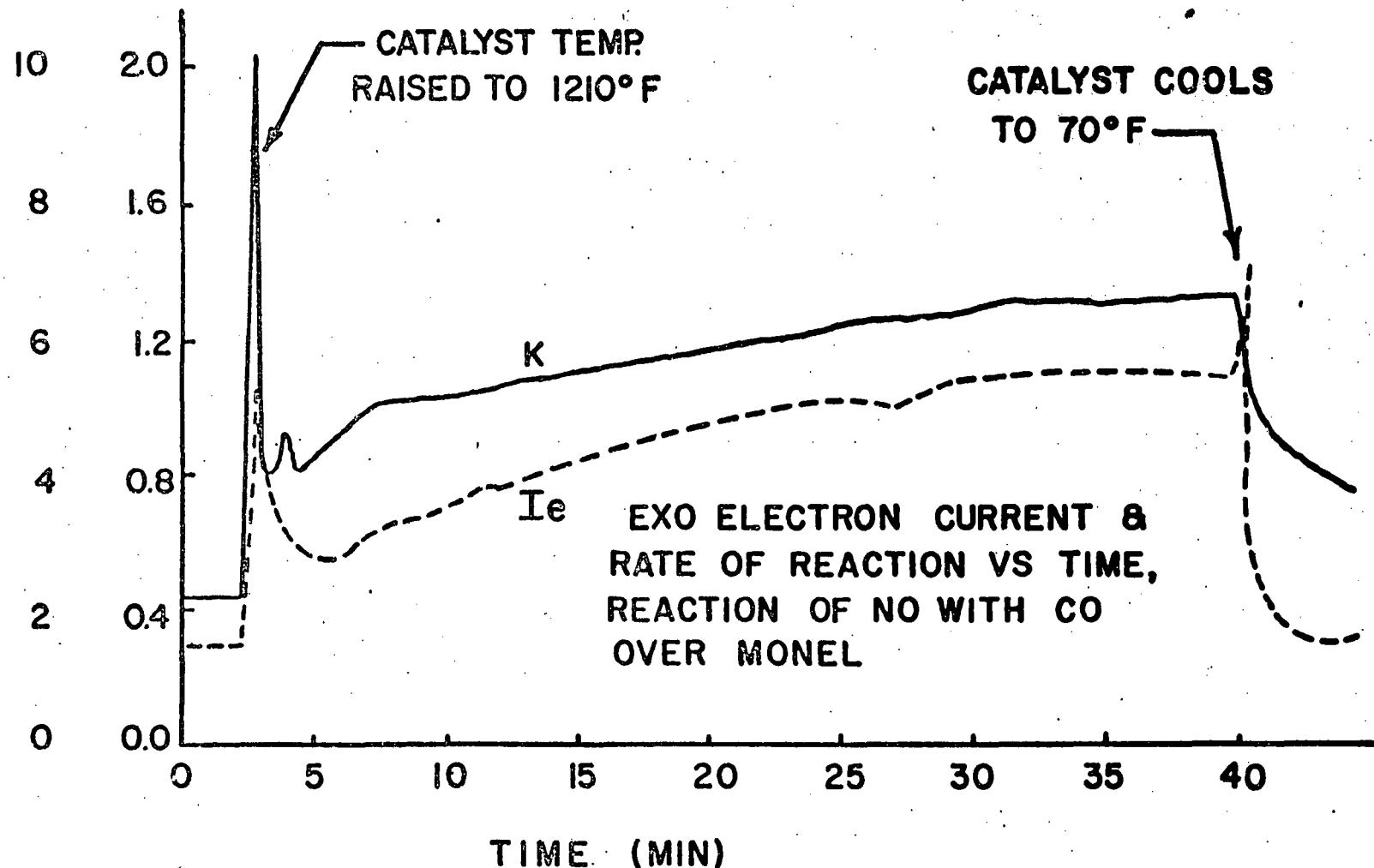




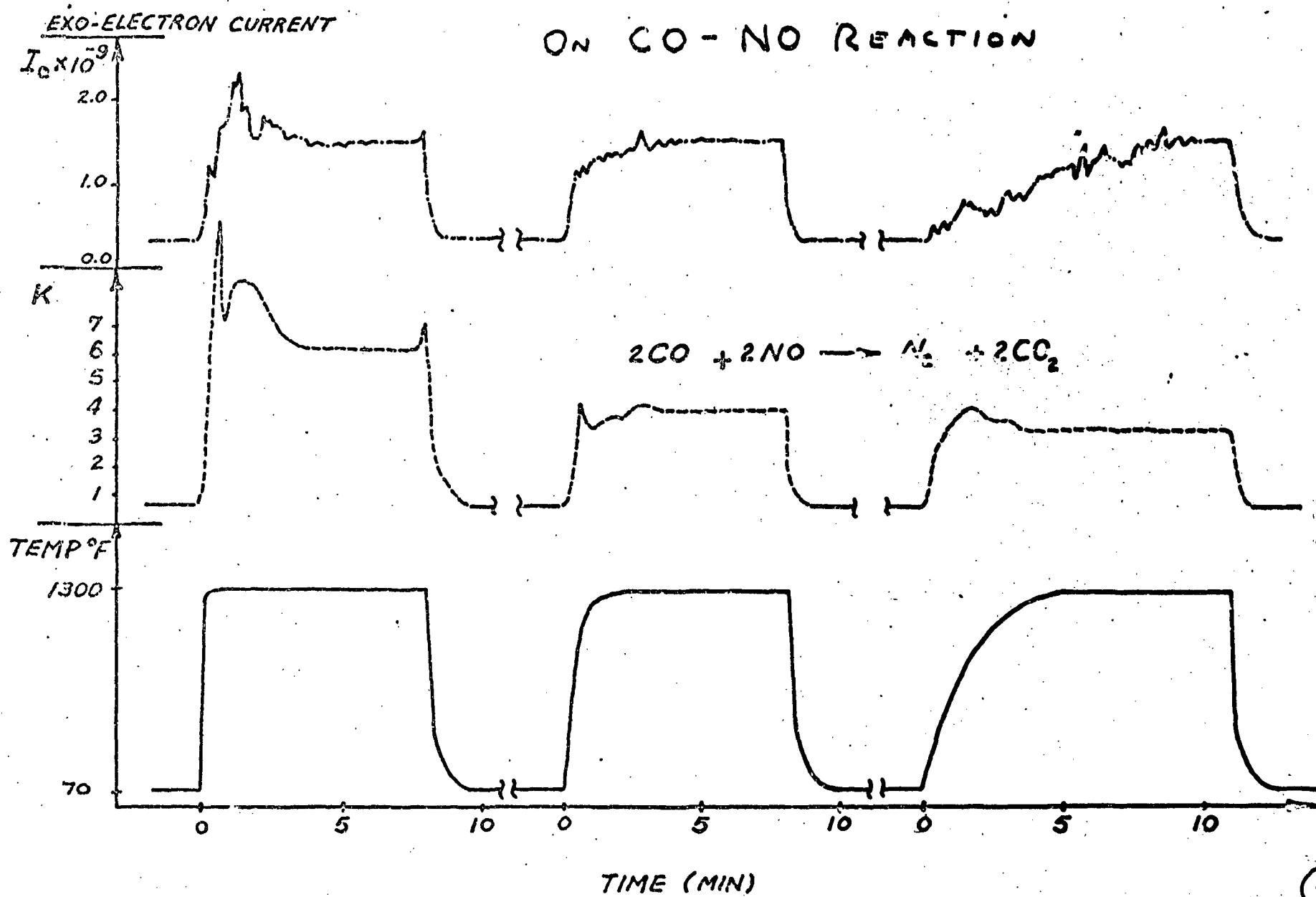
EXO-ELECTRON GRINDING SYSTEM



$K$   $I_e \times 10^{-9}$  AMPS



HEATING RATE EFFECTS  
ON CO - NO REACTION



SECOND ANNOUNCEMENT  
SYMPOSIUM ON EXOELECTRON PHENOMENA  
June 28 and 29, 1973  
RIES, WAYNE STATE UNIVERSITY  
Detroit, Michigan

This two-day Symposium on Exoelectron Phenomena will be held as planned on June 28 and 29, 1973 in the General Lectures Hall on Anthony Wayne Drive at Warren on the Wayne State University Campus in Detroit. The Symposium is organized by the Research Institute for Engineering Sciences and sponsored by the College of Engineering.

PROGRAM:

The program will consist of three sessions, each of approximately three and one half hours duration. One session will be devoted to exoelectron emission from insulators, another to emission from metals and the third to technical applications.

The following invited papers will be presented:

"Exoelectron Emission from Metals," Dr. W. J. Baxter, (General Motors).

"Applications of Exoelectron Emission in Radiation Dosimetry,"

Dr. K. Becker (ORNL).

"Experimental Techniques in Exoelectron Emission," Dr. P. Bräunlich (Bendix).

"Theory of Exoelectron Emission from Insulators," Dr. P. Kelly (National Research Council, Canada).

"Applications of Exoelectron Emission to Non-Destructive Testing,"

Dr. S. A. Hoenig (University of Arizona).

In addition there will be about fifteen contributed papers. On the afternoon of the second day, attendees will have the opportunity to visit facilities at Bendix Research Laboratories in Southfield, Michigan and General Motors Research Laboratories in Warren, Michigan.

ABSTRACTS:

We wish to remind the speakers that the deadline for the submission of abstracts is June 1. These should be clearly typed (double spaced) on one page (8½ x 11) with a 1" margin and should include title, author(s) and affiliation.

ACCOMODATIONS:

Rooms have been reserved for the nights June 27 and 28 at the Sheraton-Cadillac Hotel in Detroit. These are available at a special reduced rate for

conferees, when booked through the Conference Committee. Please indicate your requirements on the enclosed form which should be returned by June 15. Payment is to be made at the hotel.

TRANSPORTATION:

A limousine service is available from Detroit Metropolitan Airport to the hotel. A free bus service will be provided between the hotel and Wayne State University Campus each day.

PARKING:

Parking is available in a University Parking Structure on Anthony Wayne Drive just above Warren Avenue. The cost is 50 cents.

BANQUET:

A dinner will be held at 8p.m., June 28, preceded by a complimentary cocktail hour. The cost of the banquet tickets is \$8.

REGISTRATION:

Registration is scheduled from 6p.m. to 8p.m. in the Sheraton-Cadillac Hotel on June 27 and on June 28 from 8:30a.m. to 9:00a.m. at the General Lectures Hall. Since the registration fee of \$20 includes luncheon each day, it would be appreciated if the enclosed form be returned before June 15.

International Conference in Czechoslovakia

The response has been insufficient to organize a group flight to Prague for the International Exoelectron Conference.

The Organizing Committee

William Baxter, G.M. Research Labs.

Peter Bräunlich, Bendix Research Labs.

Pieter K. Rol, Wayne State University

I SENT  
S 20  
IN ADVANCE

May 7, 1973

Dr. Pieter K. Rol  
Ries College of Engineering  
Wayne State University  
Detroit, Mich. 48202

Dear Dr. Rod:

I just realized that I forgot to mention my need for hotel reservations in my reply to your symposium announcement.

I would like reservations at the Sheraton-Cadillac for June 27th and 28th at the special reduced rate. The reservation for June 27th should be guaranteed for late arrival. I will pay for this in advance, if necessary.

My title and abstract is enclosed.

I will look forward to meeting you.

Yours truly,

S. A. Hoenig  
Professor EE

SAH:es  
Enc.

**Non-Destructive Evaluation of Fatigue, Grinding And  
Catalysis By Means Of Exoelectron Emission**

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**To Be Presented by Prof. S. A. Hoenig**

**Department of Electrical Engineering**

**University of Arizona, Tucson, Az. 85721**

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**I. Historical Introduction**

**Early Observations of Exoelectron Emission (EEE) and  
attempted applications. Driving Forces that induce EEE.**

**II. Applications**

**A. Fatigue and Fracture.**

**1- Emission after fatigue**

**a) Apparatus**

**b) Experimental Results With and Without  
External Heating. Prediction of the  
point of ultimate failure.**

**2- Emission During the Fatigue Process,**

**Detection of Microcrack Formation.**

**Prediction of the Point of Ultimate Failure.**

**B. Observations of Annealing After Quenching**

**Or Shot Peening**

**1- a) Apparatus**

**b) Results**

**C. Observation of Catalytic Processes**

**1- Apparatus**

**2- Results**

**D. Monitoring Grinding Processes**

**1- Apparatus**

**2- Results**